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Development of Flame Retardants for Polyester/Cotton Blends

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EXPERIMENTAL TECHNOLOGY INCENTIVES PROGRAM (ETIP)

The Experimental Technology Incentives Program was initiated in fiscal year 1973 as part of the President's program to learn how the Government could stimulate technological innovation. The objective of the program is to learn how the Federal Government can provide policies and incentives which will encourage greater technological innovation by the private sector. Broader application of innovative technology could lead to the amelioration of several national problems such as a low rate of increase in productivity, negative trade balances, environmental pollution, and public health and safety.

The interrelation of the Government and private sector is complex and not enough is known to predict the effect on technological innovation of a change in government policy. Consequently, various hypotheses regarding possible federal policy are being tested with analyses and experiments.

ETIP has identified four policy-related program areas for investigation and experimentation. These areas relate to procurement practices at all three governmental levels, regulatory practices at the federal and state levels, federal practices for the funding of civilian R&D, and federal economic assistance practices. In each of these areas, new or modified governmental policies will be tested in cooperation with the agencies responsible for implementation.

In addition, ETIP will be evaluating the impact of its experimentation on the cooperating agencies and on the commercial sector. These evaluations should result in a body of knowledge that encompasses the practices tested, any barriers encountered, effectiveness of use and potential for adoption.

The accompanying report was prepared under contract as part of the ETIP program of the National Bureau of Standards. Statements contained in this document represent the views of the originating organization and do not necessarily reflect those of the National Bureau of Standards.

Director
Experimental Technology Incentives Program
National Bureau of Standards
U. S. Department of Commerce

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TABLE OF CONTENTS

	<u>PAGE</u>
INTRODUCTION	1
PROJECT OBJECTIVES	2
ORGANIZATION OF THE CONSORTIUM	3
PROJECT ADMINISTRATION	6
OPERATION OF THE CONSORTIUM	7
INTERACTION WITH OTHER RESEARCH GROUPS	23
BACKGROUND INVESTIGATIONS	26
RESEARCH STRATEGY	27
STATE OF THE ART AS OF JUNE, 1974	28
1. Theory of Flame Retardant Action	33
2. Development of Potentially Commercial Flame Retardants	65
2a. Blending of Fire Resistant Fibers	68
2b. Chemical Aftertreatment of PET/Cotton Blend Fabrics	70
TESTING METHODOLOGY	81
1. Oxygen Index and 45° Angle Burning Tests	82
2. Calorimetric Measurements	84
3. Correlation of Test Methods	104
POLYESTER	120
1. Basic Factors Affecting PET Flammability	120
1a. Pyrolysis of Untreated PET	120
1b. Effect of Bromine on PET Flammability	127
1c. Effect of Phosphorus on PET Flammability	143
1d. Role of Condensed Phase Oxidation in PET Flammability	149
2. Flame Retardant Polyester	171
2a. Inherently Flame Retardant PET	171
2b. Grafting Studies	174

STUDIES ON POLYESTER/COTTON BLENDS	214
FLAME RETARDANT SYSTEMS BASED ON PHOSPHORUS ALONE	215
1. Antiblaze ^(R) 19	215
2. N-methylol-3-(diphenylphosphinyl) propionamide	219
3. Other Organophosphorus Retardants	242
4. Mixtures and Precondensates of Phosphorus Retardants	246
FLAME RETARDANT SYSTEMS BASED ON BROMINE ALONE	304
1. Calorimetric Evaluation of FR P-44 ^(R)	304
2. Application of FR P-44 ^(R) with Durable Press Resins	312
3. Application of FR P-44 ^(R) with a Bromine- Containing Latex	312
4. Application of Other Bromine-Containing Flame Retardants	322
FLAME RETARDANT SYSTEMS BASED ON COMBINATIONS OF PHOSPHORUS AND BROMINE	328
1. Optimization of Phosphorus-Bromine Formulations	328
2. Interaction of Flame Retardant Fibers	335
3. Phosphorus-Bromine Systems Based on Phosphonium Salts	356
3a. THPS ^(R) /Urea/PVBr and Related Systems	356
3b. Determination of Flame Retardant Efficiencies of Bromine Compounds	366
3c. Utilization of Other Bromine Compounds with Phosphonium Salts	370
4. Systems Based on a Bromine-Containing Phosphazene	385
5. Systems Amenable to Fixation by Irradiation	393
SUMMARY AND CONCLUSIONS	426
BIBLIOGRAPHY	436
INDEX	440

GLOSSARY OF CHEMICAL ABBREVIATIONS

BABA 50	bis-acrylate of 2-hydroxyethyl ether of tetrabromobisphenol-A
BDPOM	bis(2,3-dibromopropyl)phosphonyl-2-oxyethyl methacrylate
DAP	diammonium phosphate
DAVP	dimethyl 1-acetoxyvinylphosphonate
DBDPO	decabromodiphenylene oxide
DBPA	2,3-dibromopropyl acrylate
DBPM	2,3-dibromopropyl methacrylate
DEVP	diethyl vinylphosphonate
DMAP	dimethyl allylphosphonate
DMVP	dimethyl 1-methoxyvinylphosphonate
DPA	dimethylphosphonomethyl acrylate
DVP	dimethyl vinylphosphonate
H ₆ or "Hexa"	1-(1,2,3,4,7,7-hexachlorobicyclo[2.2.1]-2-hepten-5-yl)-ethene
MDMP	N-methylol-3-(dimethyl phosphinyl)propionamide
MD3P	N-methylol-3-(diphenyl phosphinyl)propionamide
NDPA	N-(dimethylphosphonomethyl)acrylamide
OBBP	octabromobiphenyl
PCHDT	poly(1,4-cyclohexylene dimethylene terephthalate)
PCPM	pentachlorophenyl methacrylate
P(DBPA)	poly(2,3-dibromopropyl acrylate)

GLOSSARY OF CHEMICAL ABBREVIATIONS (con't)

PVBr	poly(vinyl bromide)
P(VBr/VC1)	vinyl bromide/vinyl chloride copolymers
TBBPA	tetrabromobisphenol A
TBPA	2,4,6-tribromophenyl acrylate
TBPM	2,4,6-tribromophenyl methacrylate
TBPOEA	2,4,6-tribromophenoxy ethyl acrylate
TBPOEMA	2,4,6-tribromophenoxy ethyl methacrylate
TBPP	tris(2,3-dibromopropyl) phosphate
THP	trihydroxymethyl phosphine
T23P	tris(2,3-dibromopropyl) phosphate
TPP	triphenylphosphate
TPPO	triphenylphosphine oxide
VBr ₂	vinylidene bromide

List of Tables

<u>Table No.</u>	<u>Title</u>	<u>Page No.</u>
I	Heat of Combustion of Polyester and Cotton Cellulose	49
II	Reaction Rate Constants and Activation Energies of the Thermal Degradation of PET	61
III	Comparison of Top and Bottom Oxygen Index Methods	83
IV	Comparison of Flammability Test Methods	85
V	Calorimetric Parameters of Various Treated Systems	92
VI	Isoperibol Results of Polyester/Cotton Blends	95
VII	Isoperibol Results of Diammonium Phosphate Treated 50/50 Polyester/Cotton	98
VIII	Calorimetric Data of Decabromodiphenyl Oxide Treated Fabrics with Fiber-Glass-Grid Support	100
IX	Char Length in cm as a Function of Mode of Ignition and Exposure Time. ETIP 50/50 Polyester/Cotton	106
X	Char Length as a Function of Exposure Time for ETIP 50/50 Polyester/Cotton with Several Precondensate Based Finishes	108
XI	Calorimetric and MAFT Data for Some Selected Fabrics	109
XII	Calorimetric and MAFT Data for F.R. Treated Fabrics	110
XIII	Char Length (FF-3) and OI on Treated 100% Cotton Fabrics	114
XIV	Flammability of Fabrics Treated with Fyrol 76 [®]	115
XV	Flammability of Fabrics Treated with Pyroset [®] TK-115	116
XVI	Flammability of Fabrics Treated with FR P-44 [®]	117
XVII	Flammability of Flame Retardant Treated Polyester Fabrics	118
XVIII	Flammability Behavior of Polyester Single Knits Treated with 15% Tanatard [®] DN-2	119
XIX	Polyester Samples Prepared for Flammability Studies	121
XX	Thermogravimetric Weight Loss and Melting Point of Polyesters	124
XXI	Oxygen Index of Polyesters	125
XXII	Thermogravimetric Weight Loss Analysis and Oxygen Index of Copolymers and Homopolymer Mixtures	128
XXIII	Summary of Linear Regression Analysis of Isoperibol Calorimetry Results	138

List of Tables (cont.)

<u>Table No.</u>	<u>Title</u>	<u>Page No.</u>
XXIV	Hydrogen Bromide Release of Bromine Fire Retardants	140
XXV	Thermal Analysis of Bromine Fire Retardants	144
XXVI	P Containing Additives and/or Comonomers in PET	147
XXVII	Flammability of Diammonium Phosphate Treated Polyester	148
XXVIII	Comparison of Rate Constants, k, For Different Configurations of PET in Varying Oxygen Environments at 356°C	150
XXIX	The Effect of Oxygen on the Decomposition Rate, k, of Dacron® 54 Poly(Ethylene Terephthalate)	152
XXX	Comparison of the decomposition rate constants, k, for Dacron® 54 and deep-dyeing PET	154
XXXI	Rate Constants for the Decomposition of Dacron® 900F and the Comparison to Dacron® 54	156
XXXII	Decomposition Rate Constants for Phosphazene-containing PET (PFR)	158
XXXIII	Comparison of TGA and ESR Data for PET Decomposition	168
XXXIV	Cyclophosphazene Physical Properties	172
XXXV	Flame Retardant Efficiency of VBr or PET as a Function of Location	192
XXXVI	Monomers Grafted	193
XXXVII	Physical Properties of Grafted PET	195
XXXVIII	Tenacity and Elongation Vs Copolymer Graft	196
XXXIX	Thermogravimetric Analysis of Grafted Polyester	200
XL	Typical Data on Grafted PET Fibers	202
XLI	Initial Grafting Results on PET Fabric	206
XLII	Flame Retardant Efficiency as a Function of Thermal Stability	209
XLIII	Grafts with No Low Temperature Decomposition Point	210
XLIV	Maximum Thermal Stability of Polymer Repeat Units	211
XLV	Effect of Phosphonium Precondensates on PET Flammability	212
XLVI	Flammability of Blends Treated with Antiblaze® 19	216
XLVII	Isoperibol Calorimetry Results from Antiblaze® 19 Treated 50/50 Polyester/Cotton Blend	218

List of Tables (cont.)

<u>Table No.</u>	<u>Title</u>	<u>Page No.</u>
XLVIII	100% Cotton Fabric Treated with MD3P (Unfixed)	226
XLIX	50/50 PET/Cotton Treated with MD3P (Unfixed)	227
L	100% Cotton Fabric Treated with MD3P (Fixed)	233
LI	50/50 PET/Cotton Treated with MD3P (Fixed)	234
LII	Isoperibol Results of DAP/Antiblaze [®] 19 Treated 50/50 Polyester/Cotton Blend	247
LIII	Flammability of Blend Fabrics with MCC-100/200/300 [®]	251
LIV	Burn Data from Fabrics Treated with Phosphorous Combinations	256
LV	³¹ P n.m.r. Chemical Shifts and Electronic Integrals	265
LVI	³¹ P Chemical Shifts of Some Selected Phosphoramides	267
LVII	Calorimetric Results From ETIP 50/50 Blend Fabric Treated with THPC/Urea and (NH ₄) ₂ HPO ₄	270
LVIII	Calorimetric Results From the ETIP 50/50 Blend Fabric Treated with Pyrovatex [®] 3762	271
LIX	Calorimetric Results From the ETIP 50/50 Blend Fabric Treated with Combination Flame Retardants THPC and Pyrovatex [®] CP, THPC and Pyrovatex [®] 3762	272
LX	Calorimetric Results From the ETIP 50/50 Blend Fabric Treated with THPC-MCC-100 [®] Oligomer	273
LXI	Calorimetric Results From the ETIP 50/50 Blend Fabric Treated with THPOH-MCC-100 [®] Oligomer	274
LXII	Calorimetric Results From the ETIP 50/50 Blend Fabric Treated with THPC-CH ₃ NH ₂ Oligomer	275
LXIII	Calorimetric Results From DuPont 50/50 P/C and 50/50 900F [®] /Cotton Blend Fabrics with the THPC-CH ₃ NH ₂ Oligomer	276
LXIV	Calorimetric Results From the ETIP 50/50 Blend Fabric Treated with a THPS [®] (MCC-100 [®]) Urea Precondensate	283
LXV	Durability of MCC-100 [®] /THPC/UREA Finish on 50/50 Blend	286
LXVI	Durability of Oligomeric THPC/MCC-100 [®] Finishes	287
LXVII	Pad Bath THPC/MCC-100 [®] (Prepared under Non-Oxidizing Atmosphere)	290

List of Tables (cont.)

Table No.	Title	Page No.
LXVIII	Pad Bath THPS [®] /MCC-100 [®] (Prepared Under Non-Oxidizing Atmosphere	291
LXIX	Pad Bath THPS [®] /MCC-100 [®] Neutralized	292
LXX	Pad Bath THPS [®] /MCC-100 [®] Neutralized	293
LXXI	Pad Bath THPOH/MCC-100 [®]	294
LXXII	Pad Bath THPC/MCC-100/200/300 [®]	295
LXXIII	Pad Bath THPC/MCC-100 [®] /Guanidine Carbonate	296
LXXIV	Pad Bath THPC/MCC-100 [®] /Guanidine Carbonate	297
LXXV	Pad Bath THPS [®] /MCC-100 [®] /Guanidine Carbonate	298
LXXVI	THPS [®] /MCC-100 [®] Aerotex [®] 23 on ETIP 50/50 Polyester/Cotton	299
LXXVII	THPS [®] /MCC-100/200 [®] On ETIP 50/50 Polyester/Cotton	300
LXXVIII	Pad Bath THPS [®] /Carbamate/MCC-200 [®]	301
LXXIX	Isoperibol Data of the Decabromodiphenyl Oxide (White Chemical) Treated Polyester/Cotton Blends	305
LXXX	Thermal Analysis of FR P-44 [®] Finished Fabrics	309
LXXXI	Bromine Contents of Fabric Samples Treated With P-44 [®] Retardant	310
LXXXII	P-44 [®] Formulations with Permanent Press Treatments	313
LXXXIII	Flammability of Permanent Press/P-44 [®] Treatments	315
LXXXIV	Characterization of DBPA Emulsion Polymer	318
LXXXV	Physical Properties of 50/50 Blend Treated with FR P-44 [®] and P(DBPA)	319
LXXXVI	Pad Bath Formulation for P-44 [®] with P(DBPA) Based on 91% Wet Pick-Up	320
LXXXVII	Emulsifier Formulation	323
LXXXVIII	Application of Citex [®] BT-93 to 50/50 Blend Fabric	324
LXXXIX	Citex [®] BT-93 and Sb ₂ O ₃ on 50/50 Blend Fabrics	325
XC	Characterization of 50/50 Blend Fabrics Treated with Citex [®] BT-93	326
XCI	Calorimetric Data of 50/50 Blend Treated with DAP/TBPP (With Fixed TBPP)	330
XCII	Calorimetric Data of Polyester/Cotton Blends--Comparison of Calorimeters	337

List of Tables (cont.)

<u>Table No.</u>	<u>Title</u>	<u>Page No.</u>
XCIII	Calorimetric Data of Some Experimental Polyester/ Cellulose Blends	340
XCIV	Isoperibol Data of 900F [®] /Cotton Blends With Various Fabric Weight and Construction	343
XCV	Isoperibol Data of H ₃ PO ₄ Treated 900F/ Cotton Blends	344
XCVI	Char Yields of H ₃ PO ₄ Treated 900F [®] /Cotton and Polyester/Cotton Blends	345
XCVII	Isoperibol Data of 900F [®] /Cotton Blends With Varying Bromine Content	352
XCVIII	SRRC formulation	357
XCIX	Isoperibol Data of PVB/THPC and VBr/THPC Treated Blends	360
C	Heat-balance in Flame Retardant Treated Cotton Systems	363
CI	Linear Regression of Heat Release From P-44 [®] Treated Fabrics	368
CII	Linear Regression of Net Heat Reduction from P-44 [®] Treated Fabrics	369
CIII	P-53 [®] Treated Fabrics (w/o Grid Support)	371
CIV	Efficiencies of P-44 [®] and P-53 [®] Treated Fabrics	373
CV	Efficiencies of Bromine - Containing Retardants	375
CVI	Formulation for THPS [®] /P(DBPA) Finish	379
CVII	Test Data on THPC - Latex Treated Fabrics	380
CVIII	Pad Bath Formulation I for Phosphonium Condensate and P(DBPA)	382
CIX	Pad Bath Formulation II for Phosphonium Condensate and P(DBPA)	383
CX	Effect of Some Selected Additives on the Film Proper- ties of Sandoz 1030/190 with Resin and Accelerator	390
CXI	Electron Beam Fixation of P and Br Containing Monomers	394
CXII	Flammability of Cotton Fabrics Grafted with Vinyl Bromide	398
CXIII	Electron Beam Grafting Results	401
CXIV	Electron Beam Grafting Results - NDPA Copolymers	402
CXV	Electron Beam Grafting of NDPA Copolymers without Preswelling	403

List of Tables (cont.)

<u>Table No.</u>	<u>Title</u>	<u>Page No.</u>
CXVI	Effect of NDPA on Copolymerizability of Monomers	404
CXVII	Effect of Preswelling on Grafting and Flame Retardant Efficiencies	408
CXVIII	Electron Beam Grafting of Phosphorus Monomers with DBPA	409
CXIX	Grafting Using Monomer Emulsions	410
CXX	Emulsion NDPA/TBPM (50/50) PET/Cotton Fibers γ -Radiation Vacuum	411
CXXI	Durability of Fabrics Grafted Using Neat Monomer Mixtures	413
CXXII	Durability of Fabrics Grafted Under N ₂ Using Monomer Emulsions	414
CXXIII	Durability of Fabrics Grafted in Air Using Monomer Emulsions	415
CXXIV	Effect of Grafting Parameters on Durability	416
CXXV	Effect of Methylamine Pretreatment on NDPA/DBPA Grafting and Flame Retardance	418
CXXVI	Comparison of Grafting Sources	419
CXXVII	Selected Formulations for e ⁻ Curtain Experiments	420
CXXVIII	Durability of Samples Grafted in an e ⁻ Curtain	421
CXXIX	Dyebath Application of Flame Retardants to PET	423
CXXX	Dyebath Application of FR Monomers to 50/50 Blends	424
CXXXI	Durability of FR P-53 [®] Using Grafted NDPA as a Binder	425

List of Figures

<u>Figure No.</u>	<u>Title</u>	<u>Page No.</u>
1	Start-up operations	9
2	American Enka Research Plan	10
3	Hooker Chemicals and Plastics Corp. Research Plan	11
4	Polytechnic New York Operations	12
5	Southern Regional Research Center Research Plan	13
6	Research Triangle Institute Research Plan	14
7	Research Plan for Clemson University and the University of Maryland	15
8	Commercialization Plan	16
9	Pert Program for Overall Project	17
10	Pert Program for Study of Existing FR Systems	18
11	Pert Program for Design & Synthesis of Prototype Treatments	19
12	Pert Program for Scale-up of Inherently FR Polyester Blends	21
13	Effect of moisture on OI values for cotton/PET blends.	29
14	Temperature-OI relationships for fabrics containing cotton and or PET.	31
15	DTA thermograms for textile fabrics.	32
16	Rate of heat release for cotton/PET blends.	34
17	Thermal analysis of phosphoric acid treated cellulose.	36
18	Estimated tar formation for treated cotton.	39
19	Flame retardant efficiencies of trivalent phosphorus compounds.	41
20	Flame retardant efficiencies of pentavalent phosphorus compounds.	42
21	Heats of combustion of char.	45
22	Estimated fuel formation for treated PCHDT.	47
23	Treated heat releases of H_3PO_4 PET/cotton blend fabrics.	55
24	Minimum FR content for self extinguishment in vertical test.	64

List of Figures (cont.)

<u>Figure No.</u>	<u>Title</u>	<u>Page No.</u>
25	Effect of phosphorus flame retardants on the OI of 65/35 PET/cotton blends.	66
26	Effect of phosphorus flame retardants on the OI of 50/50 PET/cotton blends.	67
27	Temperature-OI relationships for fabrics (3.4 oz./yd. ²) treated with THPC-APO.	72
28	Temperature-OI relationships for fabrics (3.4 oz./yd. ²), treated with THPOH/amide.	73
29	Temperature-OI relationships for fabrics (3.4 oz./yd. ²), treated with THPOH/NH ₃ .	74
30	Diagram of polymer fire.	88
31	Calorimetric combustion scheme.	89
32	Heat release of PET/cotton blends burned with and without support.	96
33	Heat-release of diammonium phosphate treated ETIP blend burned with and without fiber-blass support.	99
34	Heat release of P-44 treated fabrics.	101
35	Net Heat Reduction of P-44 treated fabrics	103
36	Ignition Exposure Time Tester	105
37	MAFT heat transfer as a function of fabric heat release per unit area.	111
38	MAFT heat transfer as a function of fabric heat release.	112
39	Effect of scan rate on the TGA of PET in air.	123
40	Log OI as a function of $\text{Log } \frac{1}{\text{COOH}} + 2$ for PET.	126
41	GC pyrolysis of bromine containing flame retardants.	132
42	GC pyrolysis of PET films containing bromine flame retardants.	133
43	The relationship between OI values and weight % Br in PET fabrics treated with bromine fire retardants.	135
44	Heat reduction of burning PET fabrics treated with bromine fire retardants.	137
45	Normalized ESR signal versus percent weight loss for Dacron [®] 54 at a decomposition temperature of 356°.	160

List of Figures (cont.)

<u>Figure No.</u>	<u>Title</u>	<u>Page No.</u>
46	Normalized ESR signal versus percent weight loss for Dacron [®] 54 decomposed at 387°C.	161
47	Normalized ESR signal versus percent weight loss for Dacron [®] 900F decomposed at 356°C.	163
48	Normalized ESR signal versus percent weight loss for Dacron [®] 900F decomposed at 387°C.	164
49	Normalized ESR signal versus percent weight loss for phosphazene containing PET (PFR) decomposed at 356°C.	166
50	Normalized ESR signal versus percent weight loss for phosphazene containing PET (PFR) decomposed at 387°C.	167
51	OI as a function of PFR-1 in PET.	175
52	OI as a function of the wt. % PET residue at 800°C.	175
53	SEM photomicrograph showing a cross-section of embedded PET fibers.	185
54	PET fiber cross-section partially freed from embedded medium.	185
55	Energy spectrum for x-rays emitted from a PET sample solution coated with poly(vinyl bromide).	186
56	Secondary electron image of sample yielding energy spectrum in figure 55.	186
57	Bromine L x-ray map for sample shown in figure 56 using "window" indicated in figure 55 (white portion of spectrum).	187
58	Energy spectrum from sample shown in figure 56 showing "window" on background map used for map in figure 59.	187
59	Background x-ray map obtained from cross-section shown in figure 56 using window in figure 58.	188
60	Secondary electron image from a PET fiber to which vinyl bromide has been grafted.	188
61	Bromine L x-ray map for fiber cross-section depicted in figure 60.	189
62	Secondary electron image from a PET fiber to which diethyl vinyl phosphonate has been grafted.	189
63	Phosphorus K x-ray image of the cross-section depicted in figure 62.	190
64	Enhanced version of figure 63.	190

List of Figures (cont.)

Figure No.	Title	Page No.
65	Effect of grafting on PET m.p. as measured by DSC.	198
66	Analysis of grafted PET fiber thermogram.	199
67	OI as a function of % MD3P (unfixed).	220
68	Char formation as a function of MD3P (unfixed) on cotton.	221
69	Char formation as a function of MD3P (unfixed) on 50/50 PET cotton.	222
70	Comparison of the flame retardant efficiency of MD3P (unfixed) on cotton and 50/50 PET cotton.	224
71	$\Delta H_2/(\Delta H_C^0)_F$ for MD3P (unfixed) on cotton compared to 50/50 PET/cotton.	225
72	OI of MD3P (fixed) on PET/cotton blend fabrics.	228
73	Effect of fixation on chars from MD3P treated cotton.	230
74	Effect of fixation on chars from MD3P treated 50/50 PET/cotton.	231
75	Effect of fixation of MD3P on its flame retardant efficiency.	232
76	TGA of MD3P (unfixed) on cellulose.	236
77	TGA of MD3P (unfixed) on 50/50 PET/cotton.	237
78	TGA of MD3P (fixed) on cotton.	238
79	TGA of MD3P (fixed) on 50/50 PET/cotton.	239
80	Heat release of DAP/Antiblaze [®] 19 treated 50/50 PET/cotton blend fabrics.	248
81	Y/(1-X) as a function of log % P for Pyrovatex [®] 3762 treated fabrics.	250
82	$\Delta H_2/(\Delta H_C^0)_F$ as a function of log % P for MCC-100/200/300 [®] treated fabrics.	252
83	Variation of $\Delta H_2/(\Delta H_C^0)_F$ with phosphorus content of $(NH_4)_2HPO_4$ treated fabrics.	254
84	³¹ p spectrum of THPC.	260
85	³¹ p spectrum of THPOH.	261
86	³¹ p spectrum of THPC-CH ₃ NH ₂ oligomer.	262
87	³¹ p spectrum of THPC-MCC 100 [®] oligomer.	263
88	³¹ p spectrum of THPOH-MCC 100 [®] oligomer.	264

List of Figures (cont.)

<u>Figure No.</u>	<u>Title</u>	<u>Page No.</u>
89	Comparison of ^{31}P spectra of phosphonium salt oligomers.	269
90	Generalized relation between ΔH_1 and %P for flame retardant 50/50 PET/cotton blends.	278
91	$\Delta H_1/(\Delta H_{\text{C}}^0)_F$ as a function of %P for flame retardant 50/50 PET/cotton blends.	279
92	Generalized function of ΔH_2 vs. %P for flame retardant 50/50 PET/cotton blends.	280
93	Generalized dependance of residue yield on initial P content of FR 50/50 PET/cotton blends	281
94	Variation of ΔH_1 with P content of THPC- CH_3NH_2 treated blends.	284
95	Heat release of decabromodiphenyl oxide treated blends.	306
96	Net heat reduction from decabromodiphenyl oxide treated PET/cotton blends.	307
97	Bromine contents of P-44 ^(R) treated fabrics.	311
98	Heat release from DAP/T23P treated blend fabric with constant T23P content.	331
99	Net heat release of DAP/T23P treated 50/50 blends.	332
100	Calorimetric data for optimization of P/Br finishes.	333
101	Effect of fiberglass grid on ΔH_1 of PET/cotton blends.	338
102	Rates of heat release of PET/cotton blends.	339
103	Heat release of H_3PO_4 treated 900F/cotton blends.	347
104	ΔH_1 of H_3PO_4 treated 900F/cotton and PET/cotton 50/50 blend fabrics.	349
105	ΔH_1 of H_3PO_4 treated 65/35 900F/cotton and PET /cotton blend fabrics.	350
106	Heat release of various H_3PO_4 treated 900F/cotton blends.	353
107	Heat release of various 900F/cotton and PET/cotton treated with H_3PO_4 or PBVr/THPC.	354
108	Variation of ΔH_1 with %P of PVBr and P(VBr/VCl) treated PET/cotton blends.	362
109	Dependence of $\Delta H_1/\Delta H_2$ on Br content of PVBr and P(VBr/VCl) treated 50/50 blends.	364

List of Figures (cont.)

<u>Figure No.</u>	<u>Title</u>	<u>Page No.</u>
110	$\Delta H_1/(\Delta H_{CE}^0)$ and $\Delta H_2/(\Delta H_{CE}^0)$ from PBVr and P(VBr/VCl) treated PET/cotton blends.	365
111	Heat release of P-44 [®] and P-53 [®] treated fabrics.	372
112	Net heat reduction from P-44 [®] and P-53 [®] treated fabric.	374
113	Comparison of Sandoz 1030/190 film DSC results.	387
114	TGA of Sandoz 1030/190 plus resin and accelerator film.	388
115	Heat release from Sandoz 1030 as a function of Br content.	391
116	Heat release of Sandoz 1030 as a function of wt. %P.	392
117	Effect of NDPA:BDPOM copolymer grafts of 50/50 PET/cotton TGA.	405
118	TGA data on NDPA and BDPOM homopolymer grafts on 50/50 PET/cotton.	406

INTRODUCTION

PROJECT OBJECTIVES

This project has had the dual objective of developing a commercially practicable process for rendering cotton/polyester apparel fabrics flame resistant, and evaluating the feasibility of stimulating commercially important technological innovation through the organization and federal subsidization of a consortium of academic, industrial, governmental and private non-profit research laboratories. Since there are currently no accepted criteria for judging the flame resistance of general apparel fabrics, it was decided that the technical achievements of the project should be evaluated in terms of the existing standard for children's sleepwear sizes 7-14 (FF 5-74) and the proposed Category I classification as defined by the National Bureau of Standards using the mushroom apparel flammability tester (MAFT)(1).

The evaluation of the consortium approach to conducting the research and stimulating technological innovation will be made on the basis of the degree of success or failure made toward the achievement of the technical objective.

ORGANIZATION OF THE CONSORTIUM

Because of the broad scope and the complex nature of the problem it seemed highly unlikely that any single laboratory or company could succeed in developing an appropriate commercial solution within the two year time frame required by the needs of adequate consumer protection as expressed in the Request for Proposals issued by the Department of Commerce. For this reason a consortium of interested and experienced research and development organizations was formed for the specific task of conducting an integrated and coordinated search for such a solution. This consortium was composed of investigation teams from Clemson University, the University of Maryland, the Research Triangle Institute, the Polytechnic Institute of New York, the Southern Regional Research Center of the U. S. Department of Agriculture, the Hooker Chemicals and Plastics Corporation, the American Enka Company, and United Merchants and Manufacturers, Incorporated. The Dow-Corning Corporation joined the consortium in May, 1975.

The technical administration and coordination of the various phases of the project have been the responsibility of the Principal Investigator. He has been assisted in this function by the team leaders from each member of the consortium, who sit on the project steering committee. The committee members have been:

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In addition, Mr. James H. Winger, Chief, Program for Fire Prevention-Products, National Bureau of Standards and Dr. Vivian T. Stannett, Vice-Provost, Dean of the Graduate School, and Professor of Chemical Engineering, North Carolina State University have served as advisory members of the steering committee. This committee, chaired by the Principal Investigator, met to review the progress of the individual teams and plan future investigations on a quarterly basis. All major decisions concerning the technical progress of the project were referred to the steering committee for advice and consent.

Each team leader has been responsible for supervising his team in a specific phase of the project. Although the exact work plan for each group was the responsibility of the team leader, the allocation of general areas of investigation among the teams was the responsibility of the Principal Investigator in consultation with the steering committee.

It was felt that in general no formal agreements were necessary for participation in the consortium; however, formal subcontracts were required for those groups receiving funds from the ETIP grant. Contracts were therefore drawn up and signed by Hooker Chemicals and Plastics Corporation, the Polytechnic Institute of New York, the Research Triangle Institute, and the University of Maryland. A memorandum of understanding was also developed to formalize the interaction with the Department of Agriculture.

Provision was also made to assure maximum input from companies and laboratories not formally affiliated with the consortium. Such interactions were arranged on a bilateral basis with several of the consortium members. The conduct of these relationships was considered to be the sole responsibility of the individual research team involved but the results arising from them were integrated into the total effort.

PROJECT ADMINISTRATION

OPERATION OF THE CONSORTIUM

The project was divided into two phases. The first phase consisted of a determination of the basic factors controlling the flammability of cotton/polyester blends. A series of concurrent investigations was conducted into such factors as the effect of distribution of both vapor phase and condensed phase active flame retardants among the components at various blend levels. The effects of the chemical structure of selected types of phosphorus and halogen-containing retardants was also examined. These were evaluated on both cotton and polyester and their interactions on blends studied. This information was then utilized in attempts to systematically design optimum flame retardant formulations.

In order to assure maximum utilization of the results of these mechanistic studies, a parallel and concurrent set of empirical investigations of more practical treatments was carried out. A number of currently existing semi-commercial and experimental processes were evaluated to determine their modes of action, types and causes of deficiencies and potential for modification to remove these deficiencies. Samples and experimental treatments were solicited from all segments of the industry. In addition to developing new data, these efforts allowed the utilization of the results of the theoretical studies on a continuous basis as they were developed.

Although the major emphasis of this work was directed toward blends containing normal commercial fibers, there seemed to be a good possibility that special classes of polyester fibers could be developed containing specific types and quantities of flame retardants specifically formulated for inclusion in blends which would require only minimal aftertreatment in fabric form. A portion of the project has, therefore, dealt with the development of such fibers and the application of special flame retardant finishes to blends containing these intrinsically flame resistant fibers.

The second phase of the project involved the actual design and development of flame retardant treatments with commercial potential. These systems have been based on the results of the previous evaluations

and theoretical investigations. Considerable emphasis was placed on such factors as treating methodology in both solution and emulsion processes and fixation methodology using both conventional pad-dry-cure techniques and radiation grafting. This work was planned with the expectation that several systems would reach this point of development in pilot plant operations and that the most promising of these would then be selected for a full-scale mill trial to demonstrate its commercial acceptability. Thus the final results from the project was expected to include one system of demonstrated commercial potential and several additional systems having considerable promise but not developed to the point of acceptability for mill operation.

The actual operation of the consortium and the division of labor among the consortium members is illustrated diagrammatically in Figures 1-8. These flow charts are intended to show the general categories of investigations undertaken by the various research teams and the interactions of these teams.

In order to establish a schedule for the completion of the various research tasks, a series of PERT diagrams were prepared. These are presented in Figures 9-12. The numbers indicated refer to the minimum, most probable and maximum projected times in weeks to complete the various phases of the work. These diagrams were prepared by the Principal Investigator and Dr. M. J. Drews, in consultation with Dr. John J. Willard of A. D. Little & Co. Dr. Willard was asked to comment on the organization and administration of the project since he has considerable expertise in this area. Comments regarding the general organization and goals of the project were also solicited from Dr. Giuiliana Tesoro.

In most cases it was possible to keep fairly close to the schedules established in the PERT diagrams. The actual design and formulation of the candidates for commercialization required more time than originally projected but this was partially due to a greater than anticipated success with the prototype systems. This meant that there were more candidates to evaluate than had been expected.

In all phases of the project the consortium seemed to operate very

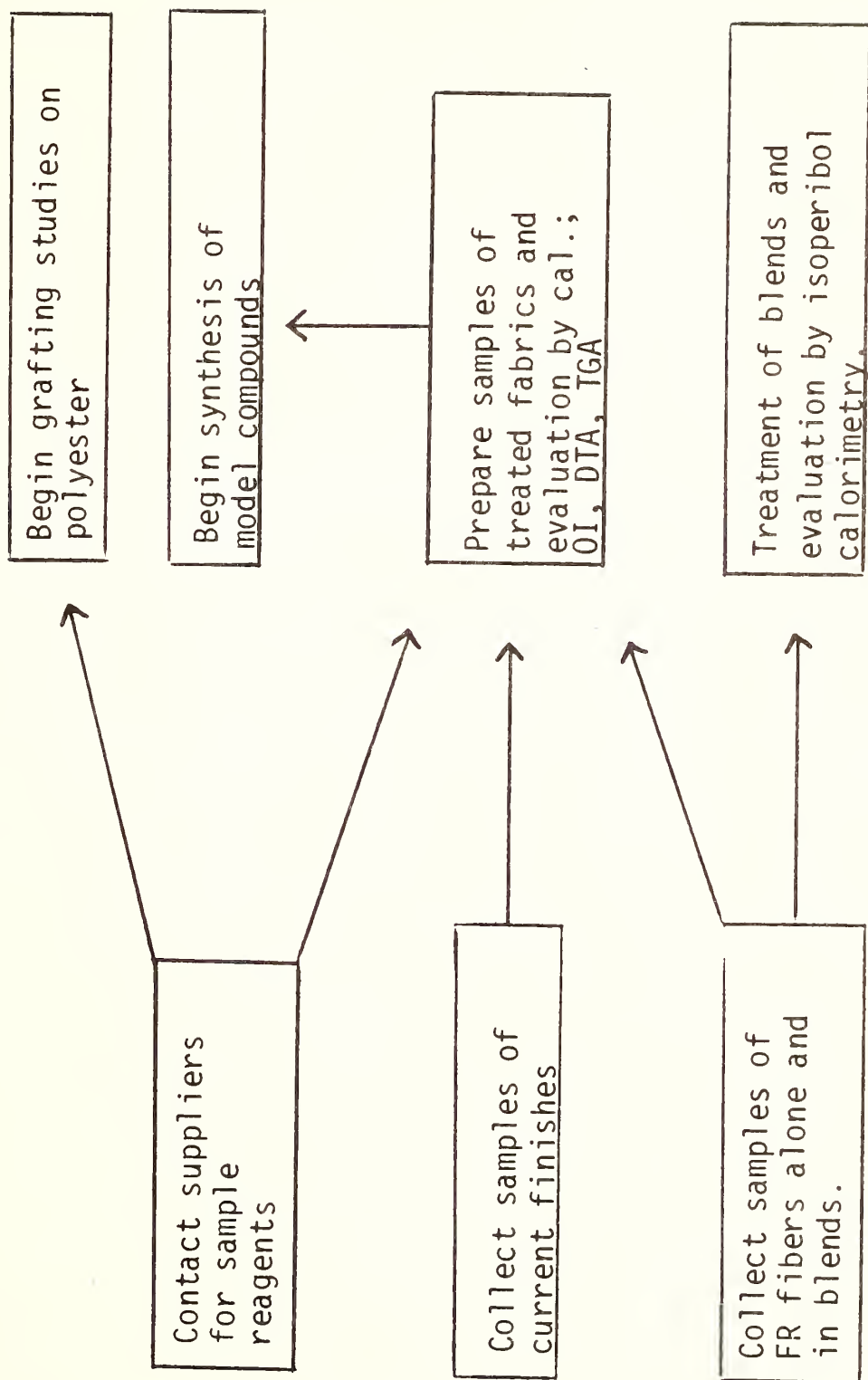
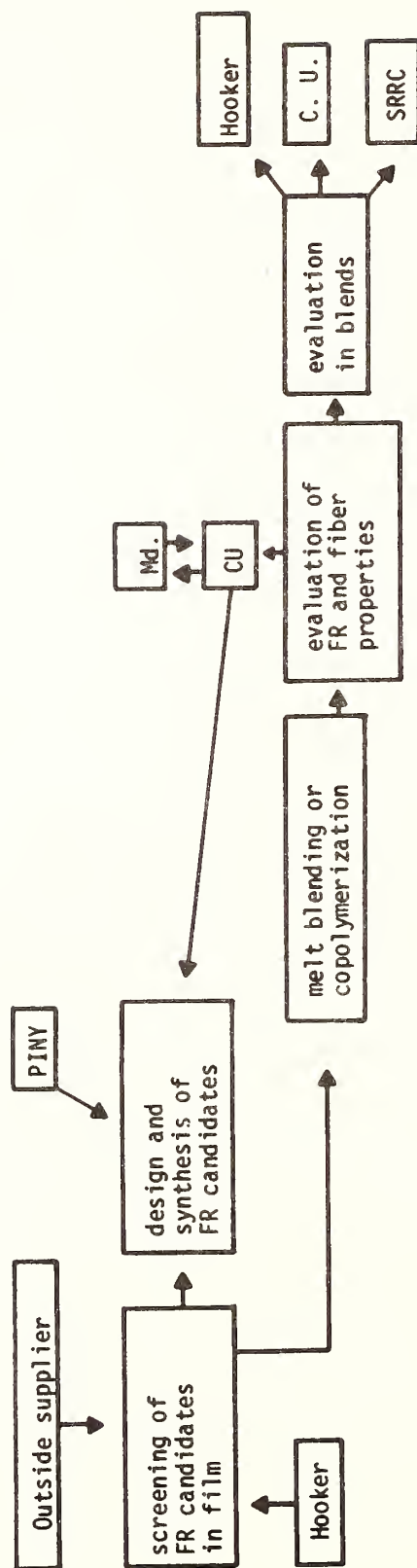


FIGURE 1. Start-up operations.

FIGURE 2
American Enka Research Plan



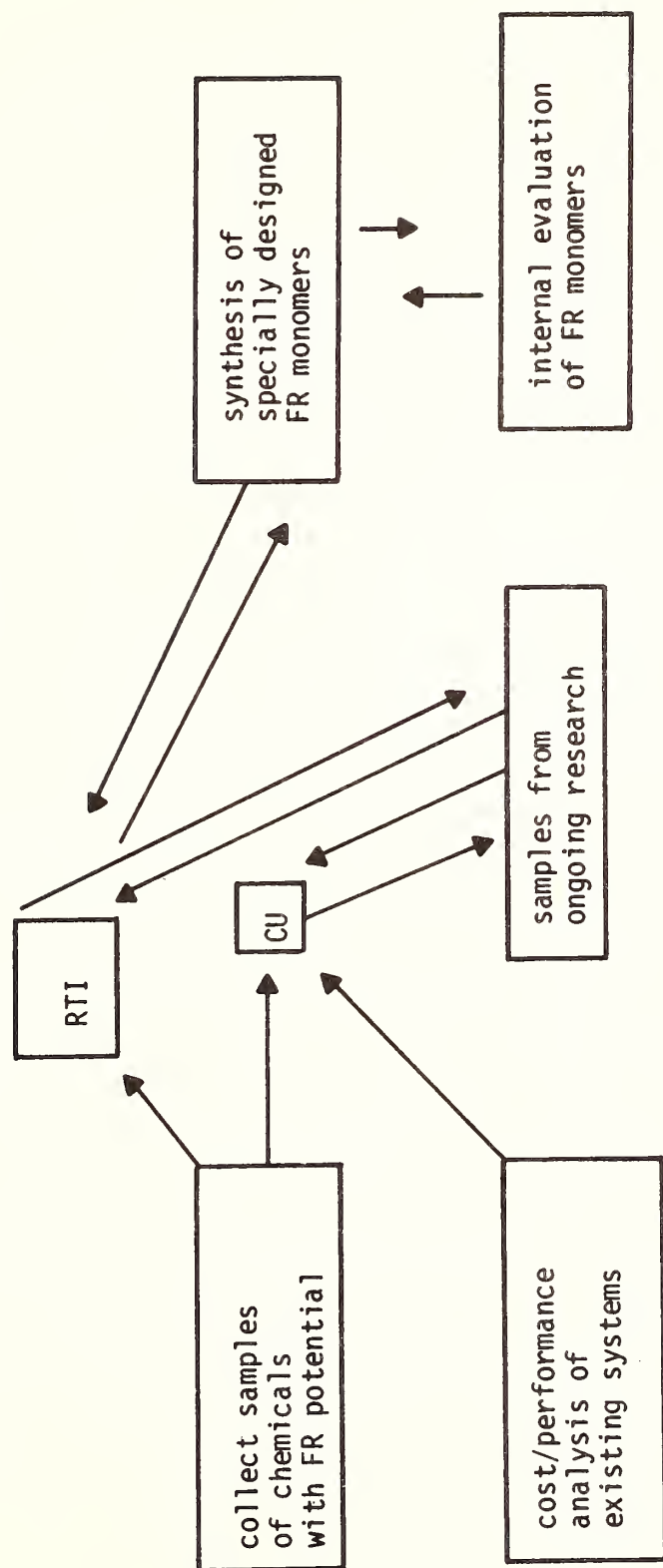
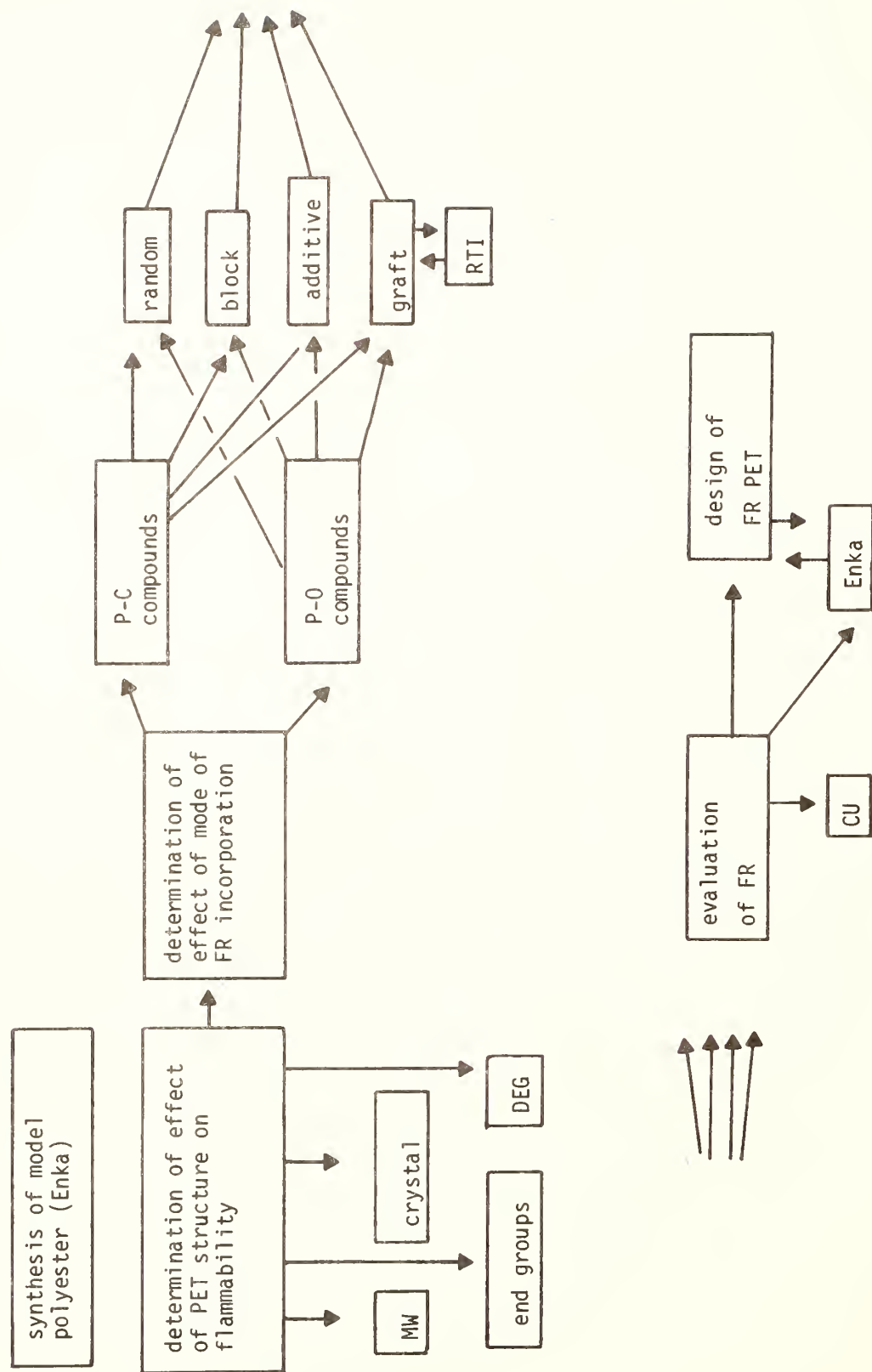


FIGURE 3. Hooker Chemicals and Plastics Corp. research plan.

FIGURE 4
Polytechnic New York Operations



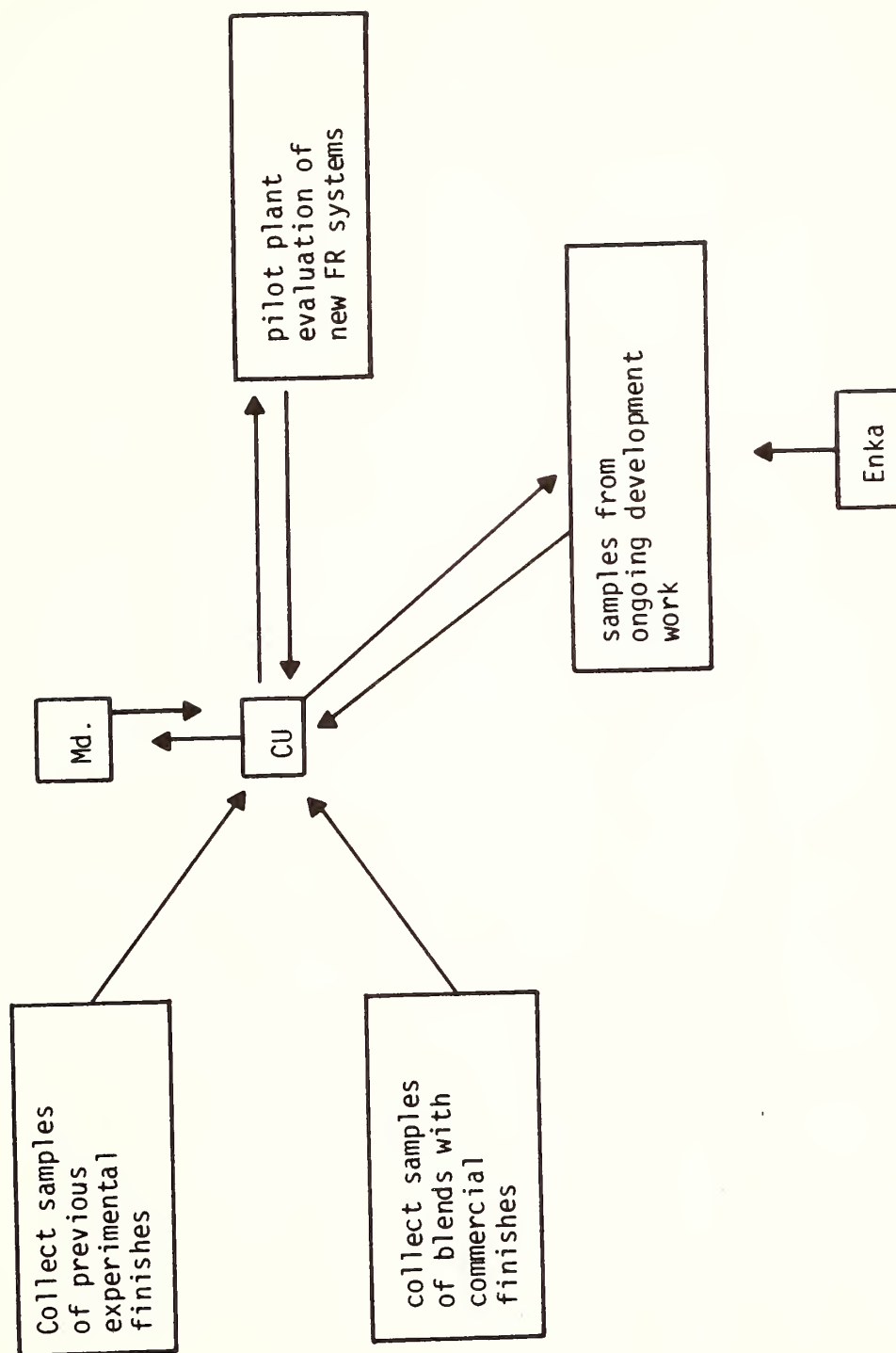
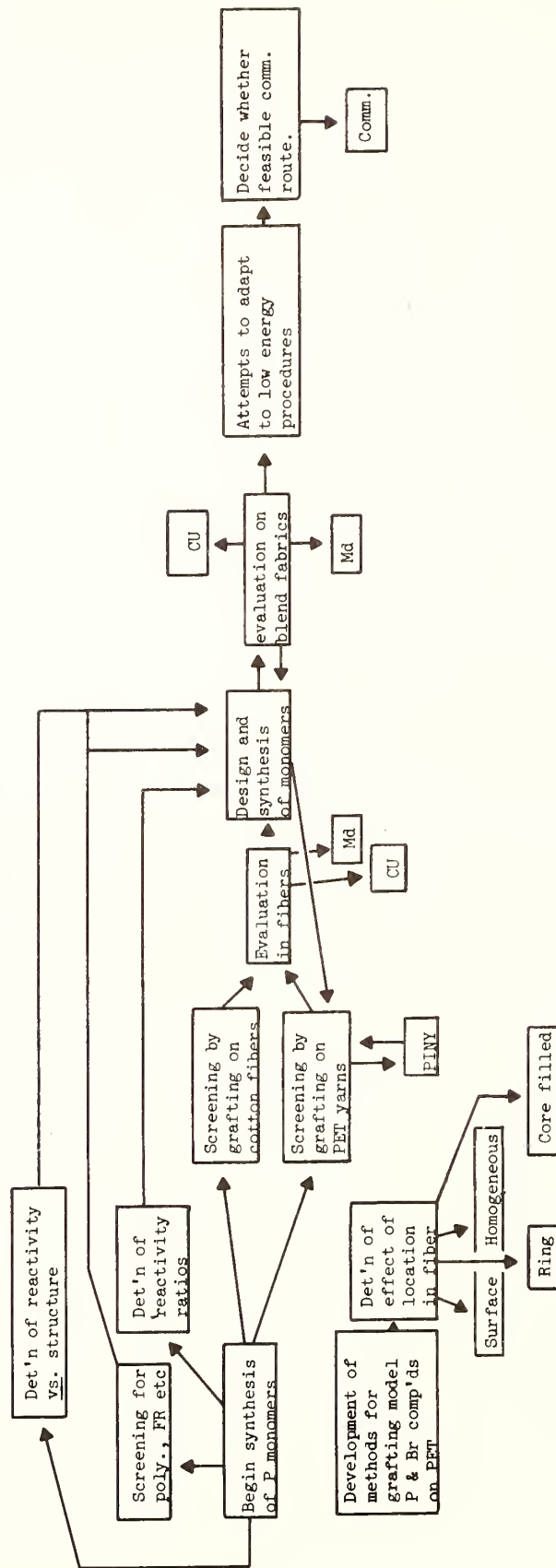


FIGURE 5. Southern Regional Research Center research plan.

Figure 6
Research Triangle Institute Research Plan



Research Plan for Clemson University and the University of Maryland

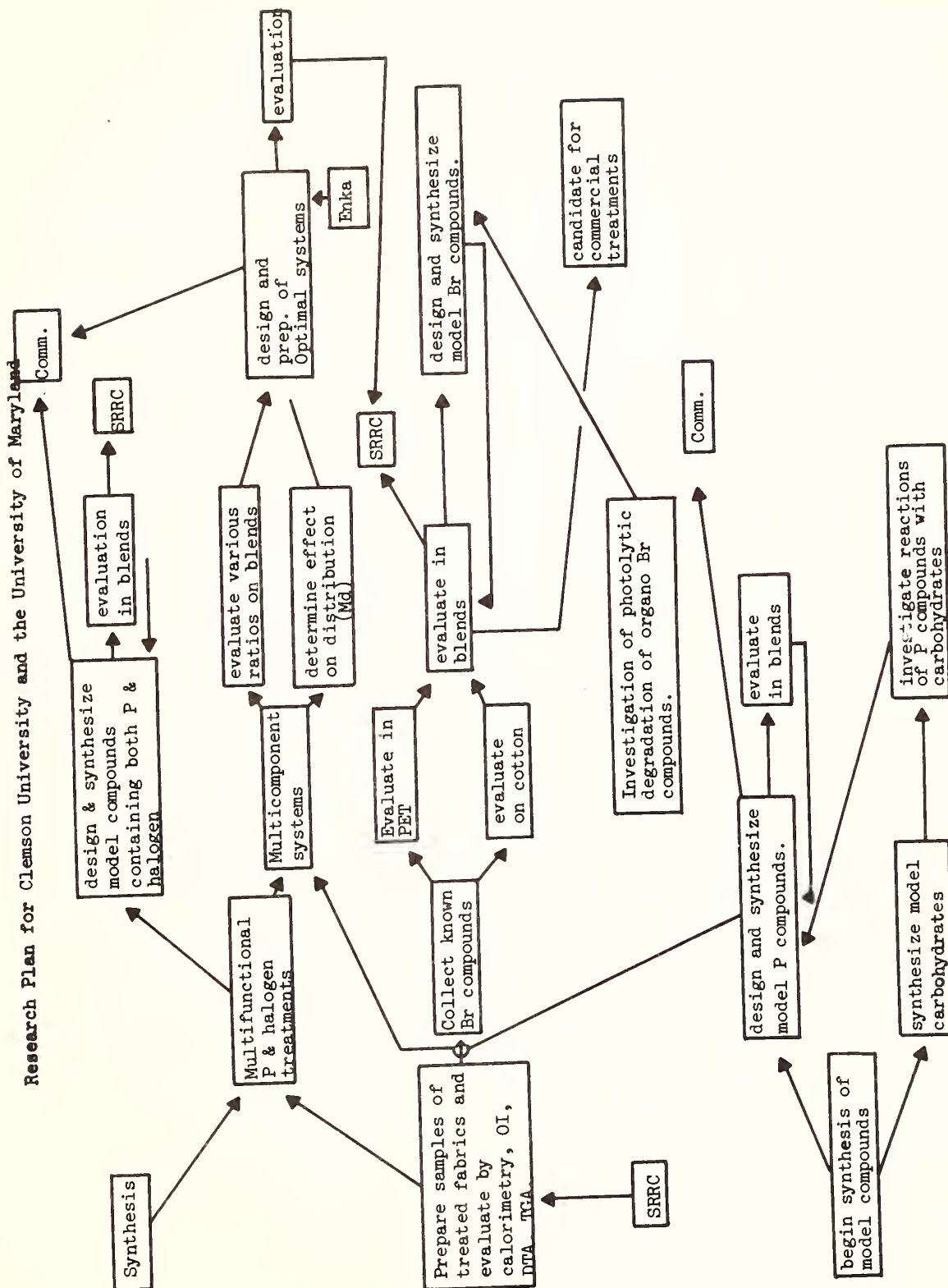


FIGURE 8
COMMERCIALIZATION PLAN

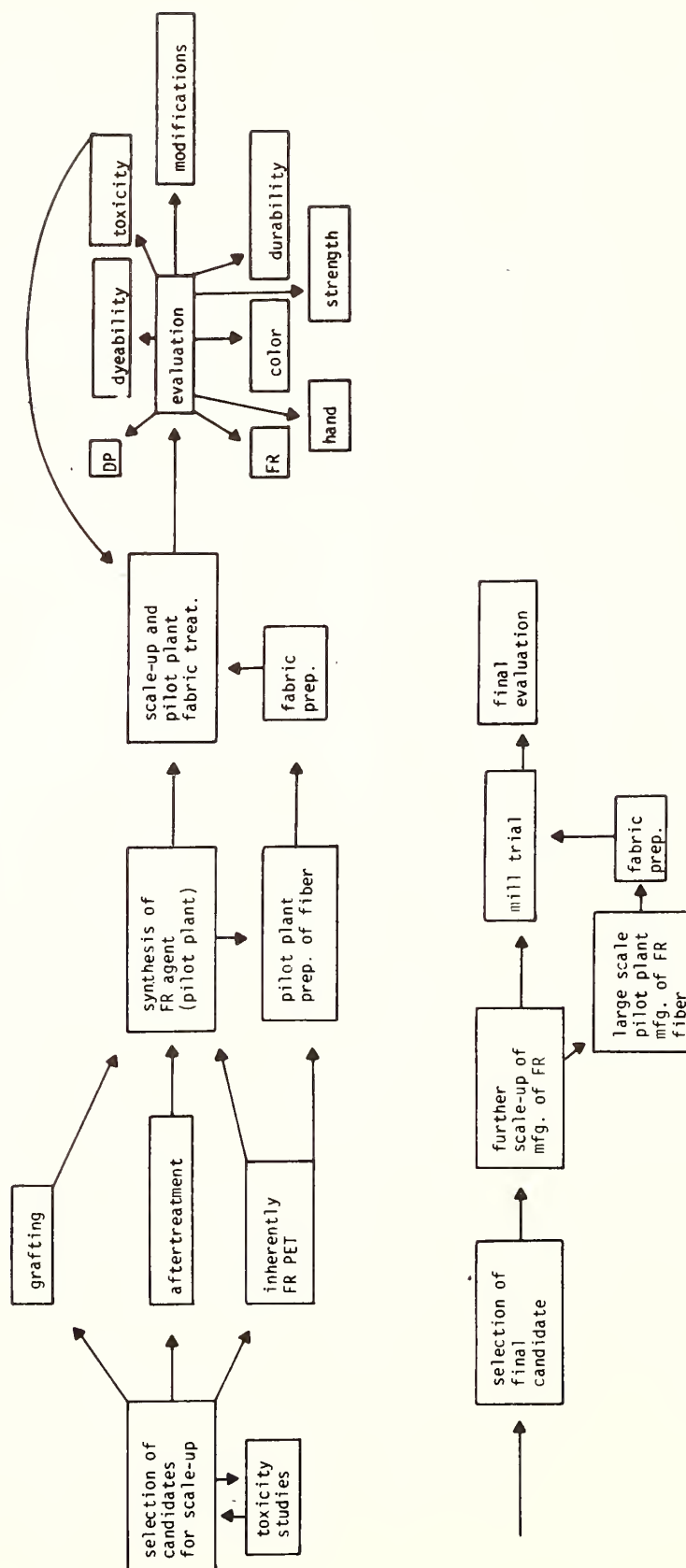


FIGURE 9

Pert Program for Overall Project

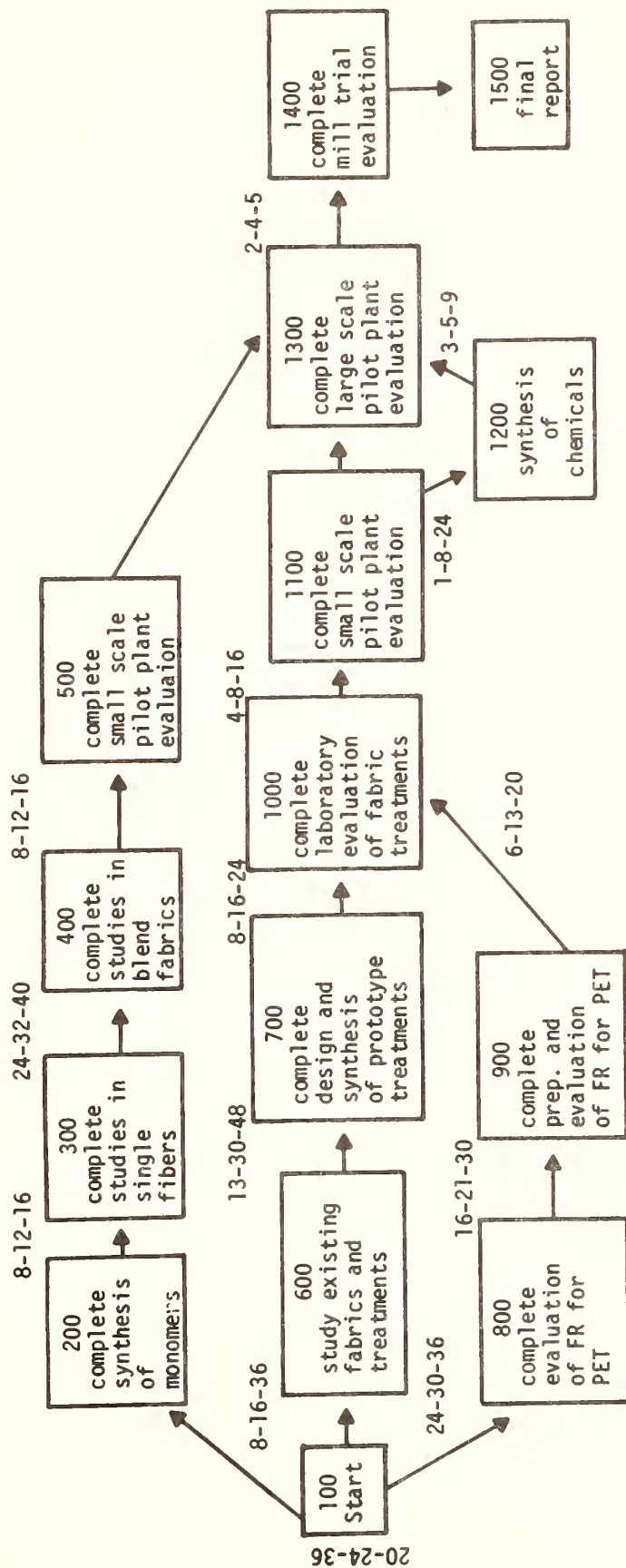


FIGURE 10
 Pert Program for Study of Existing FR Systems

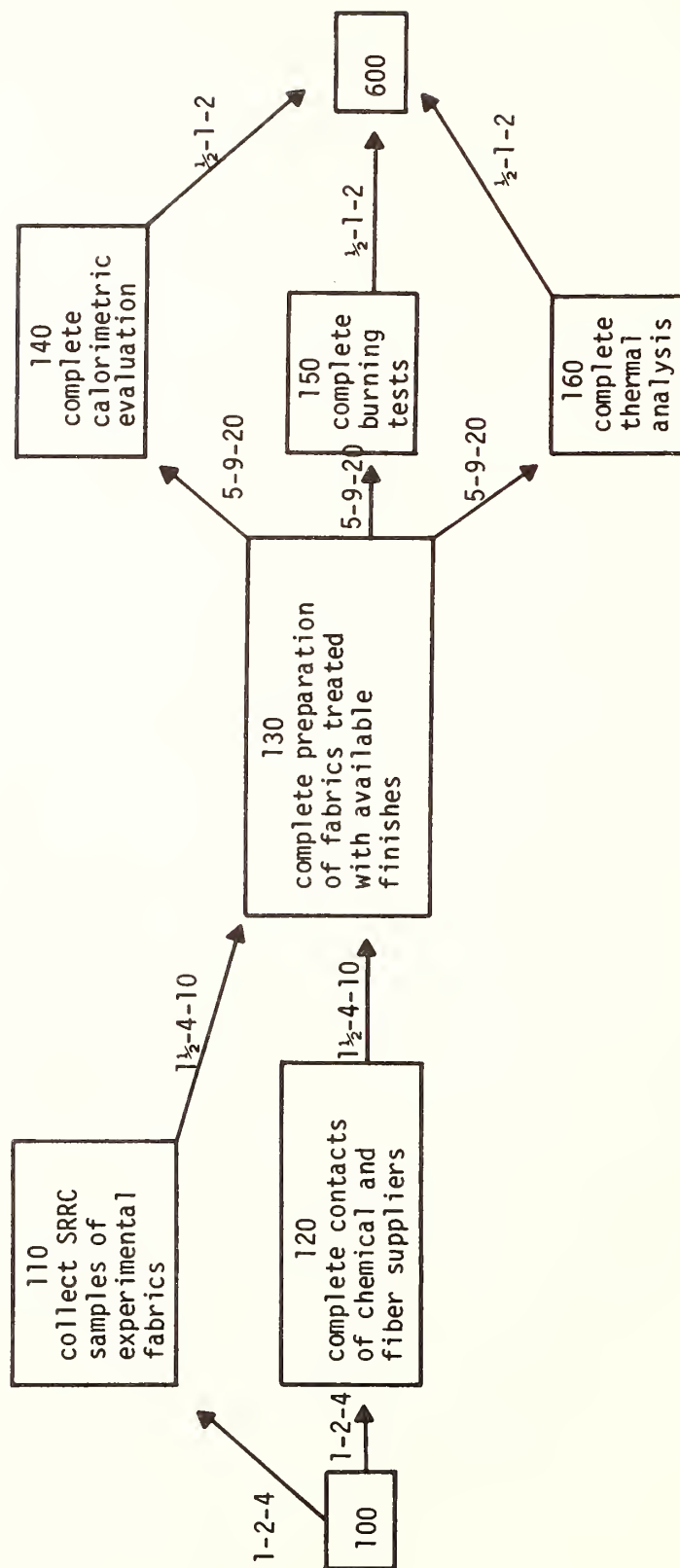


FIGURE 11

Pert Program for Design & Synthesis of Prototype Treatments

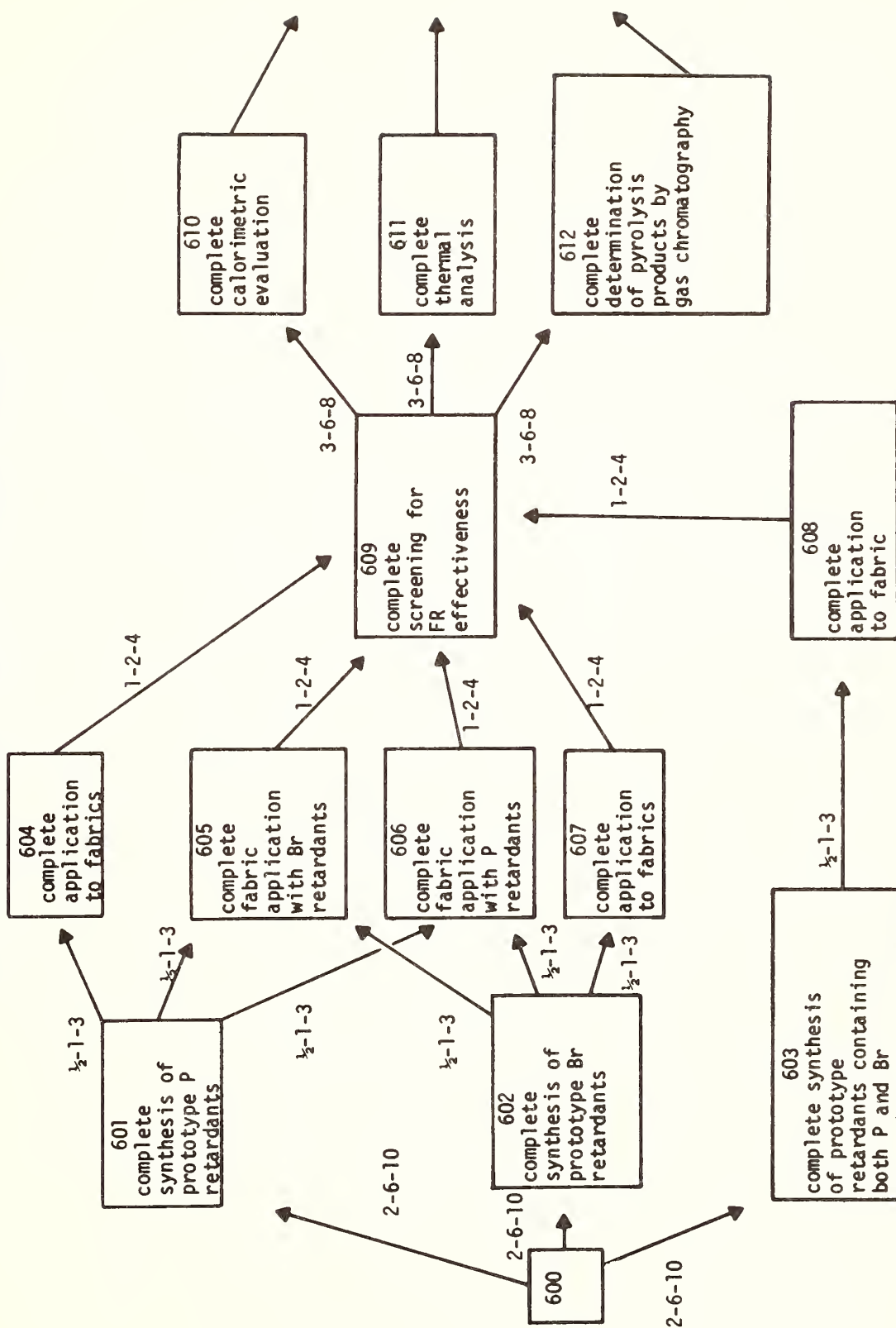


FIGURE 11 (con't.)

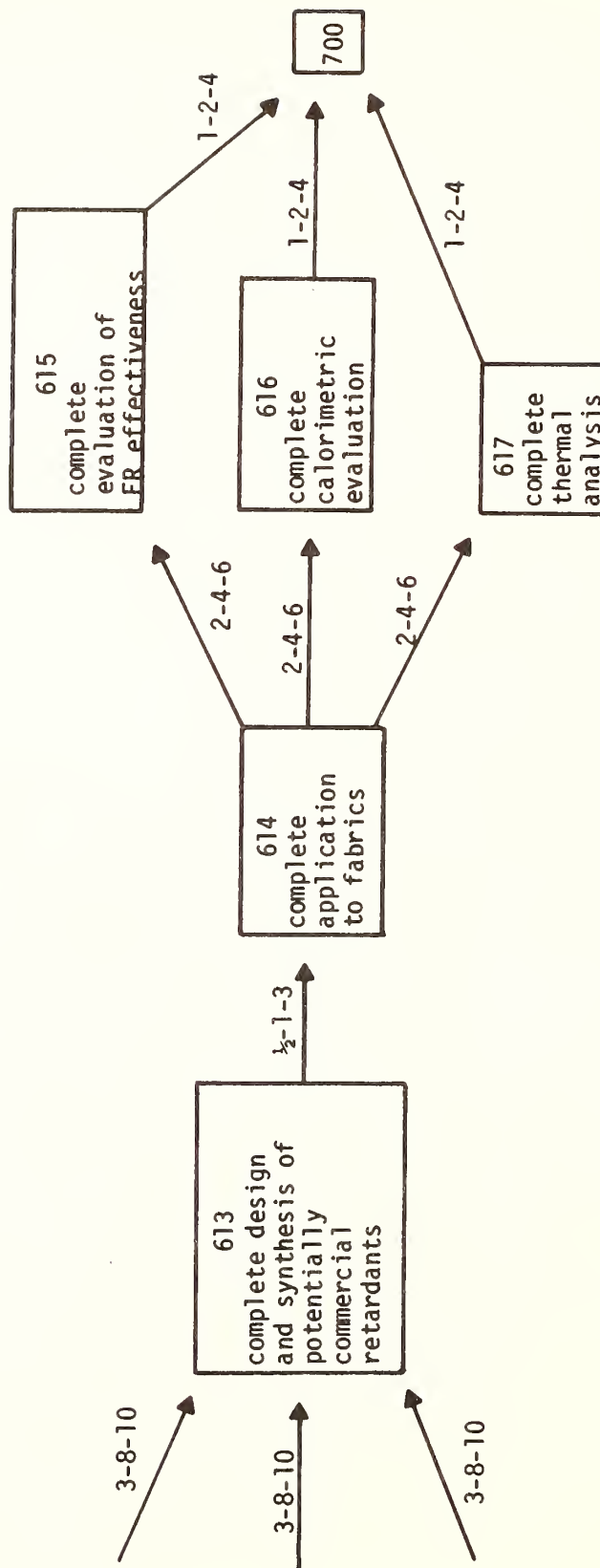
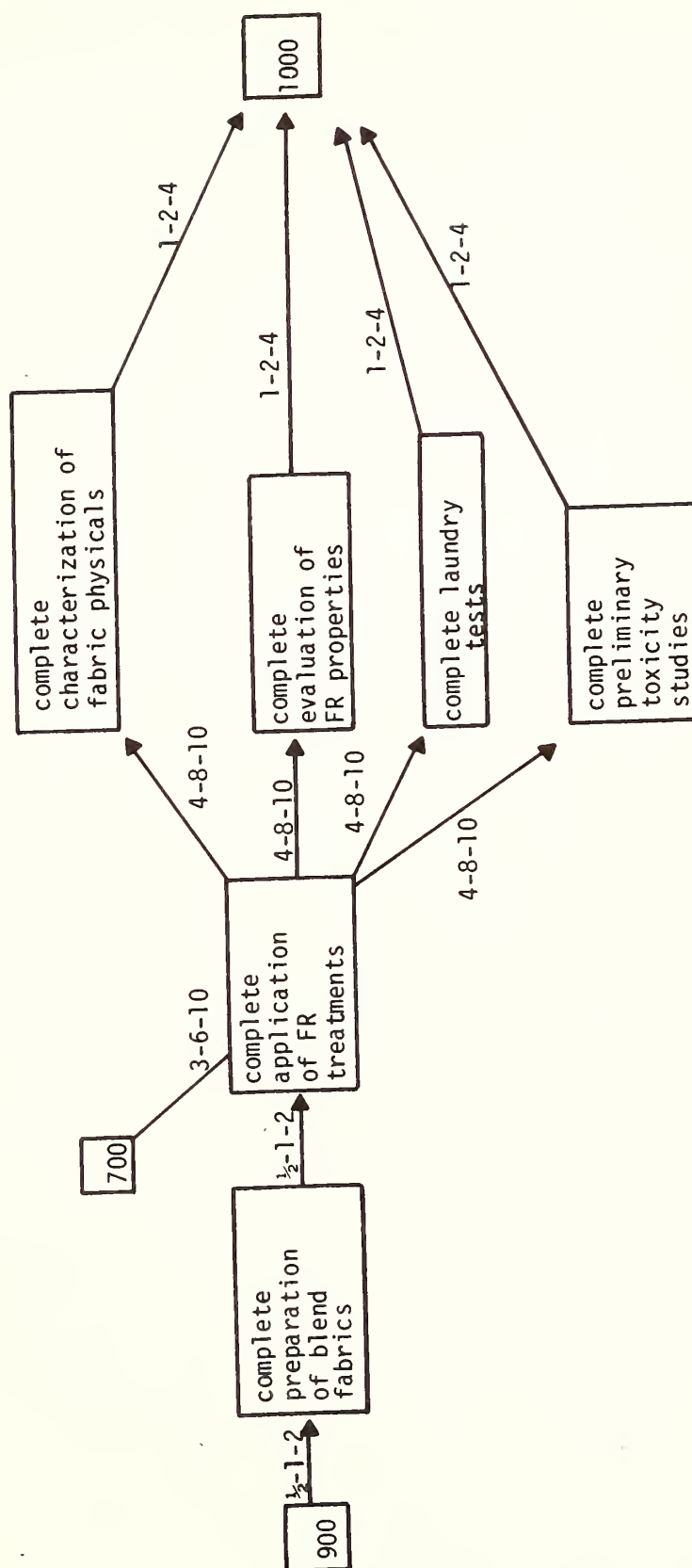


FIGURE 12

Pert Program for Scale-up of Inherently FR Polyester Blends



smoothly and the individual teams worked together very well. This was particularly noteworthy in the interactions with and among the industrial members of the consortium. Their contributions to the overall project were much greater than anticipated. In all cases the interactions between consortium members were free and open.

These results would seem to indicate that the consortium approach to research administration is a feasible and useful one. This conclusion is shared by the members of the consortium as evidenced by the recent decision of the project steering committee to continue meeting on a regular basis for at least one year following the termination of the ETIP sponsorship.

Based on the experience gain from this project it is obvious that the most important factors in determining the success of such a consortium approach are the attitudes and dedication of the consortium members.

INTERACTION WITH OTHER RESEARCH GROUPS

In addition to these interactions between the members of the research consortium, the project has generated a great deal of interest throughout the industry which has resulted in numerous inquiries from a variety of chemical, textile and fiber producers. Several companies expressed an interest in becoming involved with the consortium but upon further discussion it was discovered that potential patent problems prevented such interactions. Although it was impossible for some companies to take a specific part in the project, there has been a general willingness by chemical manufacturers and textile and fiber producers to submit samples for use or evaluation by the ETIP group.

Continuing interest in the project has been shown by many companies including Sun Chemical Company, Chester, South Carolina; Pittsburg Plate Glass Industries, Barberton, Ohio; American Hoechst Corporation, Spartanburg, South Carolina; E. I. DuPont de Nemours, Fibers Division, Wilmington, Delaware; Chas. Tanner Company, a Division of Ciba-Geigy, Greenville, South Carolina; Mobil Chemical Company, Edison, New Jersey; Great Lakes Chemical Corporation, West Lafayette, Indiana; Ethyl Corporation, Ferndale, Michigan; Sandoz Colors and Chemicals, East Hanover, New Jersey; American Viscose Division, FMC, Marcus Hook, Pennsylvania; West Point Pepperell Company, Shawmut, Alabama; Union Carbide Corporation, South Charleston, West Virginia; Lowenstein Textile Corporation, Lyman, South Carolina; Deering Milliken Research Corporation, Spartanburg, South Carolina; Tennessee Eastman Company, Kingsport, Tennessee; J. P. Stevens and Company, Garfield, New Jersey; Monsanto Chemical Company, St. Louis, Missouri; Toyobo, Inc., New York; Michigan Chemical Company, Ann Arbor, Michigan; Riegel Textile Corporation, Ware Shoals, South Carolina; Springs Mills, Inc., Fort Mill, South Carolina; American Cyanamid Company, Bound Brook, New Jersey; Dan River, Inc., Danville, Virginia; Levi Strauss, Inc., San Francisco, California; Cities Service Company, Cranfield, New Jersey; Nyacol, Inc., Ashland, Massachusetts, and Beaunit Corporation, Research Triangle Park, North Carolina.

Many of these companies have submitted samples of flame retardants and chemical auxiliaries to be included in the consortium's studies. In several cases, the companies have become very active in working with one or more of the consortium members. For example, both FMC and DuPont expended significant amounts of both time and money to prepare special samples to assist in the fiber and flame retardant interaction studies at Clemson and the University of Maryland. Similarly, both Great Lakes Chemical and White Chemical worked with the groups at Clemson and the Research Triangle Institute to design and prepare bromine-containing compounds of special interest in the grafting experiments. Great Lakes has also donated significant quantities of bromine-containing monomers for the preparation of the latices used in several of the candidate formulations and they have arranged to have some of the preliminary toxicological studies made in these latices.

Ethyl Corporation has also provided a number of special experimental chemicals to the group and has prepared several series of specially treated fabrics for the studies of the THPC/urea/P(VBr/VCl) finish.

Both Sandoz and Toyobo have worked closely with the team at Clemson to modify the application of flame retardant systems which they had developed earlier but which had less than optimum properties for general apparel applications. A particular close relationship was formed with Sandoz and a considerable amount of joint experimentation undertaken.

A very special relationship has also been established with the research group under the direction of Professor William Walsh at North Carolina State University. His group has worked very closely with the group at the Research Triangle Institute. All of the electron beam studies carried out by the RTI investigators have utilized the NCSU equipment. In addition, Professor Walsh has been working on a separate government sponsored project which involved among other things a study of the application of Fyrol 76[®], a commercial phosphorus-containing flame retardant, by electron beam grafting; thus an informal arrangement was made under which the majority of the work with this monomer would be done at NCSU and the results made available to the ETIP con-

sortium.

Another special arrangement was made with the Research Committee of the Palmetto Section, American Association of Textile Chemists and Colorists. This group consisted of research workers from United Merchants and Manufacturers, M. Lowenstein and Company, the Graniteville Corporation, C. H. Patrick and Company, Emery Industries, C. S. Tanner and Company and Clemson University. The committee volunteered to take on the project of developing an emulsion in the consortium's work, and evaluating its potential for commercial application. The results of their work were made available to the consortium and were also included in a paper scheduled for presentation as part of the Intersectional Technical Paper Competition at the AATCC annual meeting in October, 1976.

BACKGROUND INVESTIGATIONS

RESEARCH STRATEGY

The research plan for this project was formulated on the basis of two fundamental theses: (1) that the solution of a problem as complex as that of polyester/cotton blend flammability needs significant input from experts in a number of different technical areas and (2) that it would probably be necessary to build a fund of basic knowledge of the chemical and physical factors controlling blend flammability and flame retardant action before attempting to design practical solutions to the problem.

This is quite different from the way that the textile industry has traditionally approached chemical finishing. Most of the currently used finishes have been developed by isolated commercial research groups using a predominantly empirical method. Although limited success in the flame retardation of blend fabrics has been realized in this way, the probability of achieving significant improvement in these treatments seemed unlikely. Instead, a concurrent series of empirical experiments coupled with a systematic investigation of the basic mechanisms through which flame retardants exert their influence was deemed to offer the greatest promise for the development of a truly practical chemical treatment. In this way, the accumulation of fundamental information should serve as the basis for directing the more practical experimentation and lead ultimately to a finish with optimum cost effectiveness and fabric properties. A close tie was envisioned between the fundamental and practical work with a constant interchange of results and ideas.

The results of this two year project bear out the validity of these two theses. In most areas where the desired interaction of research teams from various areas of experience and expertise has been accomplished, the work has been most successful in moving toward commercially feasible systems. Similarly, the efforts have been the most fruitful in those areas where the greatest fundamental understanding has been achieved and used to guide the development work.

STATE OF THE ART AS OF JUNE, 1974

Cotton/polyester blends pose a number of very special problems in dyeing and chemical finishing because the cotton is reactive and highly hydrophilic whereas the polyester is inert and highly hydrophobic. This frequently results in an uneven distribution of chemicals during finishing. The thermal and mechanical properties of the fibers are also quite different. Cotton tends to char on heating but generally maintains some structural integrity. Polyester normally melts and flows under the influence of temperatures above ca. 260⁰. If the two fibers are mixed and heated, the molten polyester frequently tends to "wick" on the cotton char resulting in the phenomenon of "scaffolding" as explained by Kruse (2). Because of these effects it is impossible to predict a priori the flammability of cotton/polyester blends on the basis of a knowledge of the behavior of the individual component fibers. Thus, Tesoro and Meiser (3) have shown using oxygen index measurements that the flammability of a needlepunched web prepared from a 50/50 blend of cotton and polyester was greater than that of either fiber alone in a similar structure. The hazard in the case of apparel is further increased by the tendency of the molten polymer to cling to the body of the person wearing the garment, thus causing severe burns on its own.

In an effort to determine more accurately the nature of the cotton/synthetic fiber blend problem, blends of cotton and polyester were studied using oxygen index (OI) technique (4) under conditions of varying moisture content and environmental temperatures (5-7). The effect of moisture on OI values was much greater at the lower levels for polyester than for the cotton or cotton/polyester blends (5). Bone-dry polyester had an OI value of 0.214 as compared to the value of 0.246 observed at a moisture content of 0.9%. With moisture contents above 1%, OI values increased essentially linearly (Figure 13). Cotton behaved quite differently, exhibiting a greater dependency of flammability on moisture at the higher moisture contents. Cotton/polyester blends responded to moisture in a manner similar to pure cotton, in-

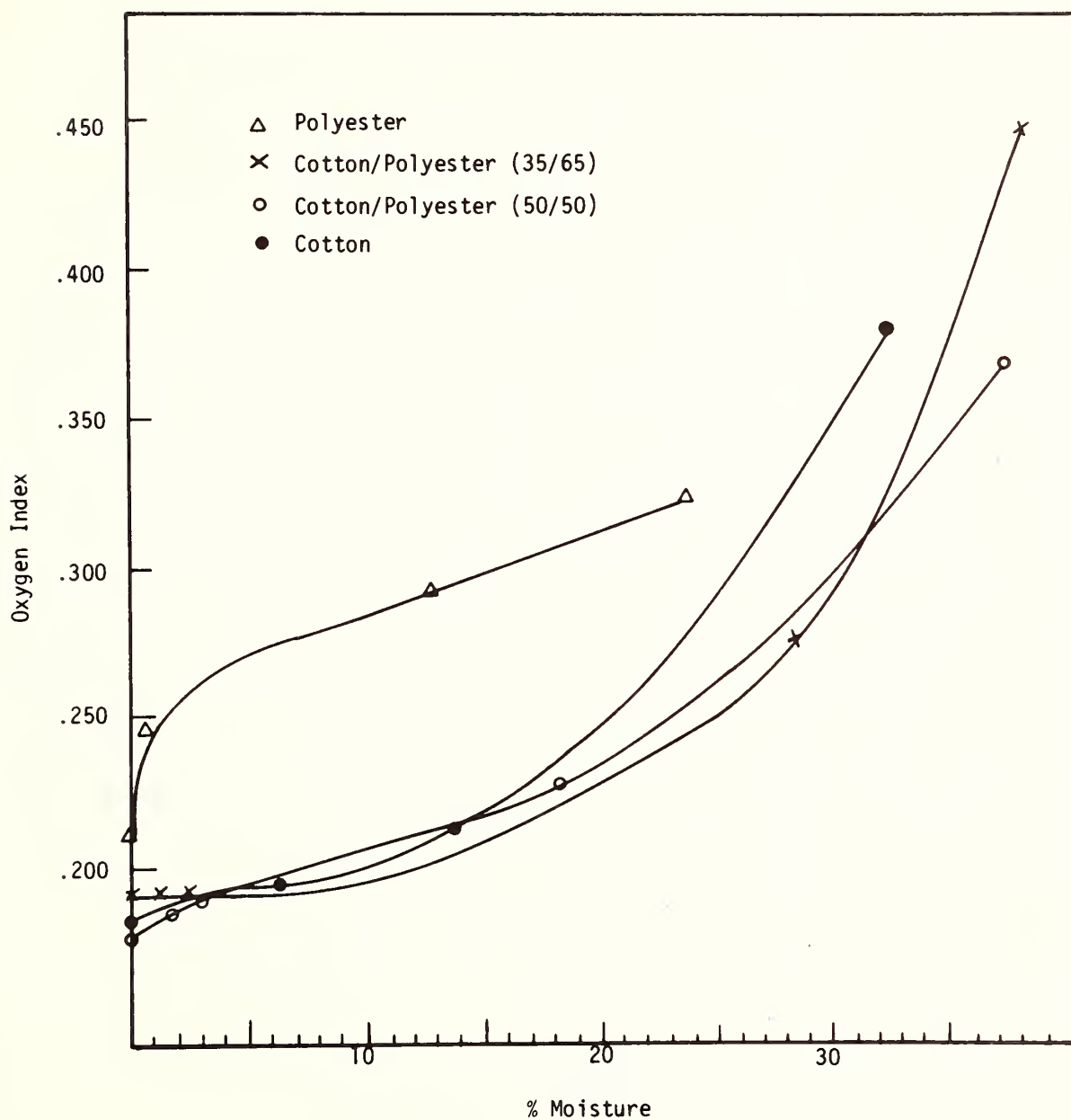


FIGURE 13. Effect of moisture on OI values for cotton/PET blends.

dicating that the dominant factor in determining flammabilities of untreated blends is the cotton rather than polyester. Closer examination of Figure 13 shows that at moisture contents less than 3%, the 50/50 blend has a lower OI value than the 100% cotton fabric. But with polyester contents greater than 50%, the OI values are slightly greater than those for cotton in the 0 to 3% moisture region. At high moisture levels (20 to 30% content) both blends were more flammable than pure cotton (5).

Hendrix and co-workers have also studied the effect of environmental temperature on the flammability of polyester and cotton/polyester blends (6, 7). Their OI data are summarized in Figure 14. From these data it is readily apparent that the cotton/polyester blends are inherently more flammable than polyester if the latter is tested without stitching. It is also apparent that the presence of the polyester in fabrics containing cotton does little to alter the variation of the OI values as a function of temperature. This latter observation has been attributed by Hendrix et al to the thermal properties of the component fibers. This is based on a study of differential thermal analysis (DTA) of the fibers and their blends as shown in Figure 15. The thermal degradation of the cotton begins at temperatures well below those required for the pyrolysis of polyester. Thus, the cotton is the initial source of fuel from the blend fabric and dictates the limits of flammability. The polyester component furnishes additional fuel to the gas phase as the polymer temperature is raised by heat produced from combustion of the cotton decomposition products. This additional fuel increases the vigor of the gas phase oxidation and thus observed burning characteristics. This is observed by a comparison of vertical downward burning rates for the two types of fabrics. A 2" x 6" sample of 100% cotton fabric required 1 minute 36 seconds to burn from top to bottom. It was observed to burn with a steady flame. The 50/50 cotton/polyester blend fabric, however, burned with a vigorous erratic flame and required only 1 minute 18 seconds to complete the burn (7).

Yeh and co-workers (8), on the other hand, have reached opposite conclusions on the basis of measurements of rates of heat release from

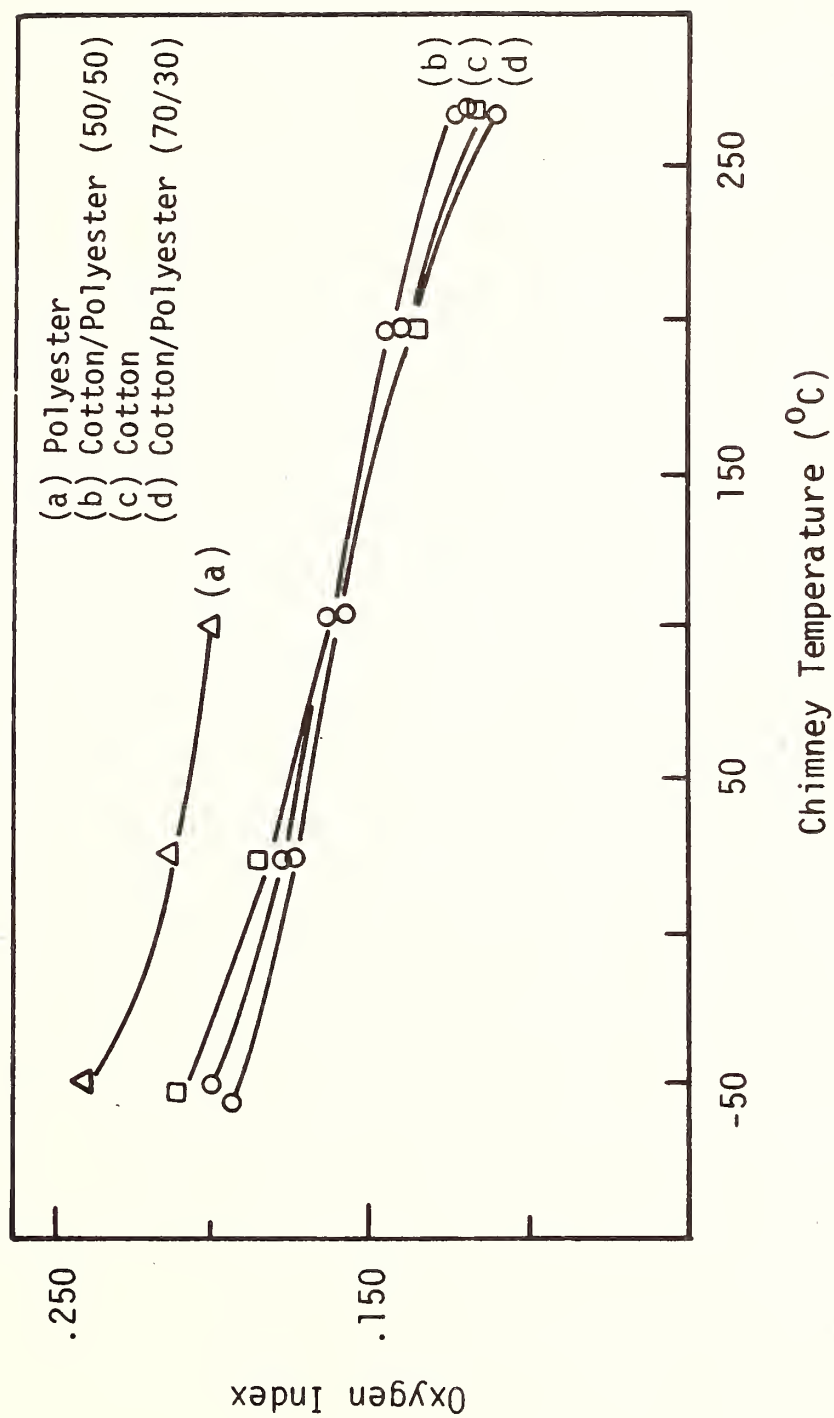


FIGURE 14. Temperature-OI relationships for fabrics containing cotton and or PET.

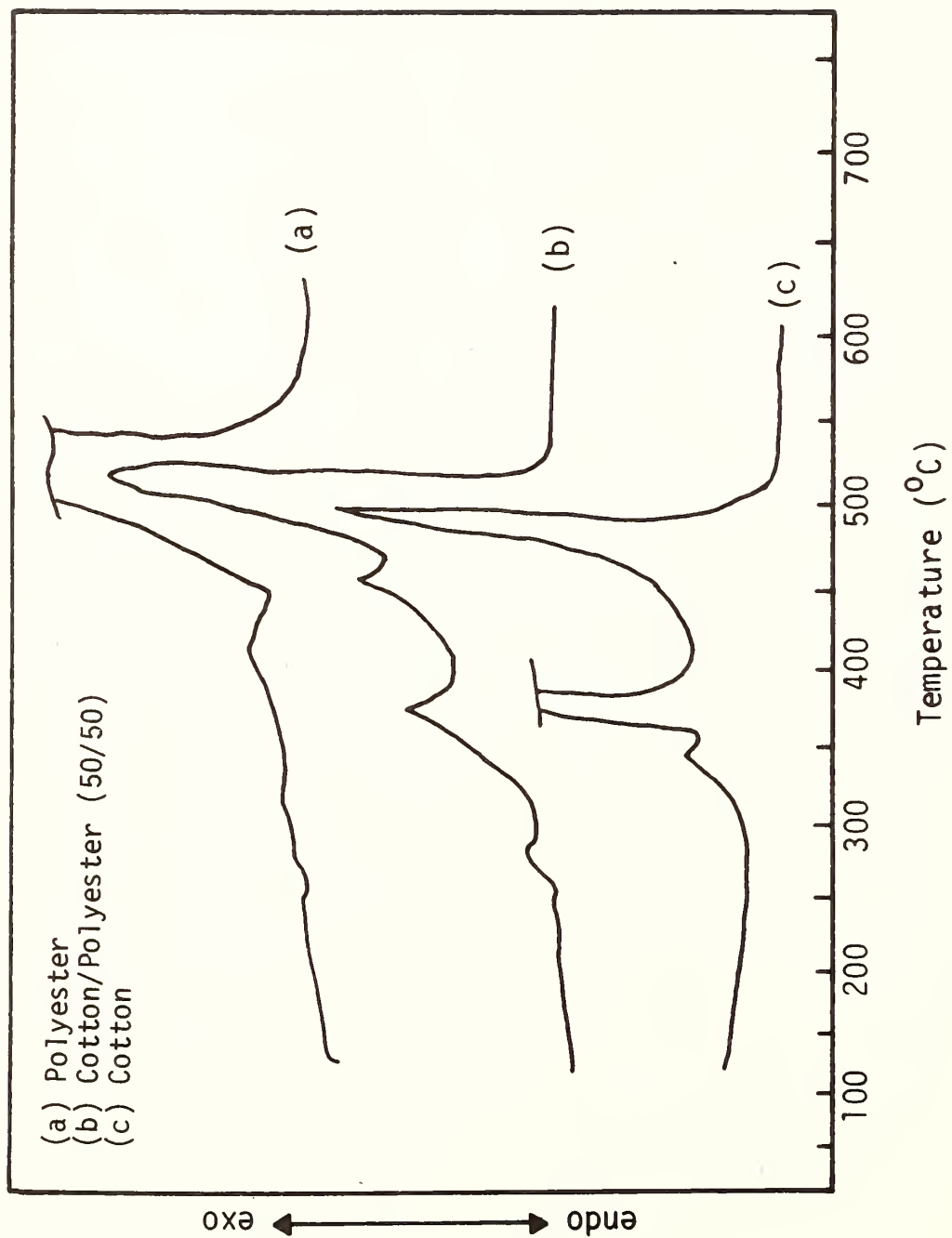


FIGURE 15. DTA thermograms for textile fabrics.

a series of cotton/polyester blends. As shown in Figure 16, the rate of heat release was found to be a direct function of the amount of cotton in the blend with pure cotton exhibiting the highest rate. Previous investigations by these same workers had shown a correlation between the rate of heat release and the rate of flame propagation.

1. Theory of Flame Retardant Action

Effective flame retardants may act either in the condensed phase or in the vapor phase above the decomposing polymer. Retardants which act in the gas phase exert their effect by functioning as either inert diluents or as free radical inhibitors which alter the oxidation processes and decrease the heat returned to the polymer surface. Those retardants which act in the condensed phase may operate by several mechanisms. They may inhibit the polymer pyrolysis so that it does not break down to produce the small volatile molecules necessary for flame propagation. More commonly, however, they act to alter rather than inhibit this thermal degradation reaction. The alteration is such that the mode of decomposition is changed and lesser quantities of flammable gas are produced. Finally, they may also exert their effect in a physical rather than chemical manner. In this case they act as a shield to prevent the transfer of heat from the flame back to the polymer surface. This reduces the rate of pyrolysis and fuel production is decreased.

In order to evaluate a particular flame retardant system, it becomes necessary to determine the mechanism of action of the various flame retardants on the substrate. This usually requires a knowledge of whether the flame retardant is gas phase or condensed phase active. Once this is known, an investigation may be begun to determine the actual chemical mechanism involved in the retardation process.

A wide variety of phosphorus-containing flame retardants are known to be effective on cellulosic substrates. Of these, phosphoric acid is one of the simplest and most effective. For many years it has been postulated that this material acts completely in the condensed phase

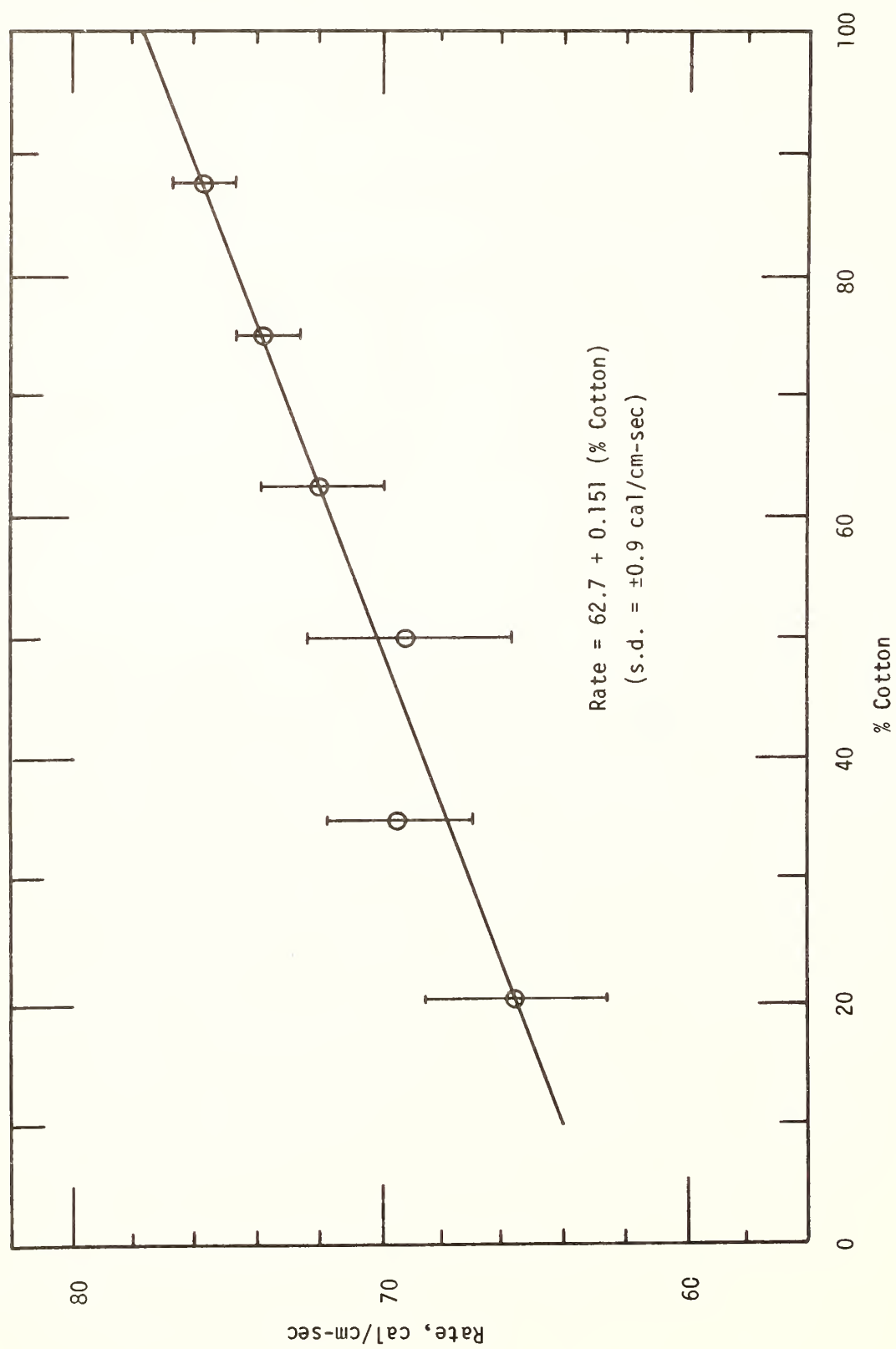


FIGURE 16. Rate of heat release for cotton/PET blends).

to alter the fuel producing reaction. That this is actually the case has been shown in a recent study (9, 10). Thermal analysis of cotton fabrics treated with various amount of phosphoric acid has been carried out. The DTA curves (Figure 17) show that the endothermic pyrolysis reaction of the cellulose occurs at progressively lower temperatures as increasing amounts of phosphoric acid are present. Under these conditions, the endothermic decomposition reaction becomes two endotherms. Similar results have been obtained with other phosphorus compounds. These endotherms have been shown to correspond to catalyzed decomposition and catalyzed phosphorylation of the cellulose (9). This is possible in the case of cellulose because of its ability to undergo decomposition by at least two competing pathways. Decomposition to carbon dioxide and water proceeds only very slowly in the absence of catalysts. In the presence of a catalyst such as phosphoric acid, however, this reaction becomes the predominant one at the expense of the fuel producing reaction.

This reduction in fuel supply is reflected in the behavior of these samples in the Oxygen Index Tester. Fenimore and Martin have suggested that the Oxygen Index Tester constitutes a good probe into flame retardant mechanisms when more than one oxidation medium is used (11). If a flame retardant exhibits similar efficiencies in two or more oxidizing agents, it is generally considered that the flame retardant does not interact with the oxidant itself, but acts only to alter the amount of fuel supplied to the flame. Measurements on phosphoric acid treated fabric using oxygen and nitrous oxide as oxidants exhibit very similar dependencies upon the concentration of retardants present as shown by the parallel lines observed when oxygen index and nitrous oxide index are plotted as a function of H_3PO_4 content of the samples. These results together with the alteration of the pyrolysis reactions observed by DTA show quite conclusively that essentially all of the phosphoric acid activity is confined to the condensed phase. However, it is necessary to use both techniques in order to reach this conclusion.

This technique has been extremely useful in studying many types of

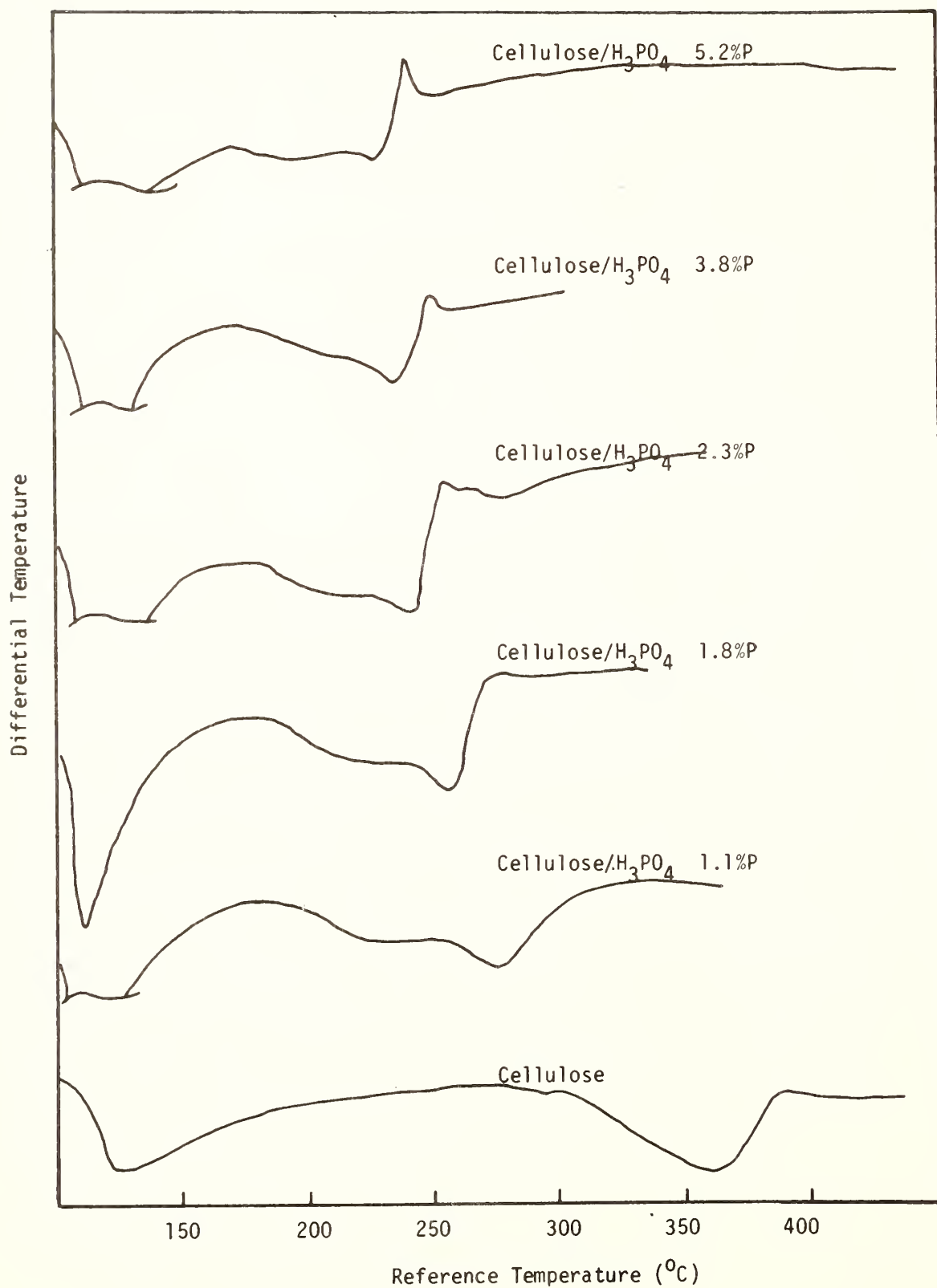


FIGURE 17. Thermal analysis of phosphoric acid treated cellulose.

flame retardants on cellulosic substrates; but it is not limited to such substrates. Triphenylphosphine oxide has been studied as a flame retardant for polyester (12). The results indicate that there is considerable vapor phase activity in this system. DTA and thermogravimetric analysis (TGA) show no differences in the decomposition of the polymer when the phosphine oxide is present. It is therefore reasonable to assume that there is no condensed phase activity exerted by triphenylphosphine oxide on polyester.

On this basis it can be concluded that thermally stable phosphorus compounds of the type exemplified by triphenylphosphine oxide act almost completely in the vapor phase. This is, of course, of considerable importance in these systems since it indicates that they will probably not produce significant alterations of the melt-drip characteristics of the thermoplastics. It also has significance in terms of smoke and carbon monoxide evolution since all of these vapor phase flame retardants act to inhibit oxidation and may therefore affect the amounts of incomplete combustion products present in the off-gases from the burning fabrics.

Although oxygen index testing and thermal analysis are frequently sufficient to gain considerable insight into fire retardance mechanisms, there are many cases where additional techniques must be used to provide enough information to allow even tentative elucidation of the fire retardant mechanism. In many such cases calorimetry provides the most useful mechanistic probe available since the net effect of a flame retardant is almost always reflected in either a reduction in the total heat produced by the burning fabric or the rate at which the heat is released. For this reason, considerable effort has been expended to develop calorimetric techniques for the measurement of such heat evolution. One of the simplest of these is based on static oxygen bomb calorimetry and involves only one major limitation (13).

When a fabric burns in open air the heat evolved cannot usually be measured directly without the aid of a specially designed isoperibol calorimeter (14); but under certain circumstances it can be calculated from more easily measureable quantities such as the standard specific

heat of combustion of the polymer and the standard specific heat of combustion of the char resulting from burning the polymer in the open air (13). This calculated value, designated as Δ , corresponds quite closely to the actual heat liberation in the case of lightweight cellulosic fabrics. This value is closely related to the total flammability of the system and is, therefore, of considerable importance. Its significance, however, lies primarily in the fact that it can be further interpreted to produce information relating to the exact molar efficiency of a particular flame retardant system. The heat value, ΔH_2 , can be related to the amount of cellulose undergoing decomposition to produce flammable gases since ΔH_2 equals the sum of Y , the weight fraction of cellulose converted to flammable gases, multiplied by the heat of combustion of the cellulose, and X , the weight fraction of reagent on the sample, multiplied by the heat of combustion of the reagent. The fraction of cellulose converted to flammable gases can then be easily calculated as $Y/(1-X)$. The dependence of $Y/(1-X)$ as a function of the concentration of the flame retardant on the fabric provides a measure of the efficiency of the flame retardant system. Using this methodology it has been possible to study the relationship between the structure of the phosphorus containing group and its efficiency in imparting flame retardant characteristics to cotton fabric. These results were the subject of several recent reports (15, 16). In addition to their significance for 100% cotton systems, these studies form the theoretical base for predicting the behavior of phosphorus flame retardants in cotton/polyester blends.

Simple phosphorus flame retardants for cellulose have been studied in this way (13). Compounds such as phosphoric acid, diammonium phosphate, and the THPOH/ammonia polymer were all found to have essentially the same efficiency characteristics as shown in Figure 18. This indicated that the limiting factor in determining the efficiency of these types of flame retardants is not their chemical structure, but rather is their ability to break down to form phosphorus oxides. These phosphorus are the common intermediates in the reaction of the retardants with the cellulose substrate. The ultimate efficiency of such non-

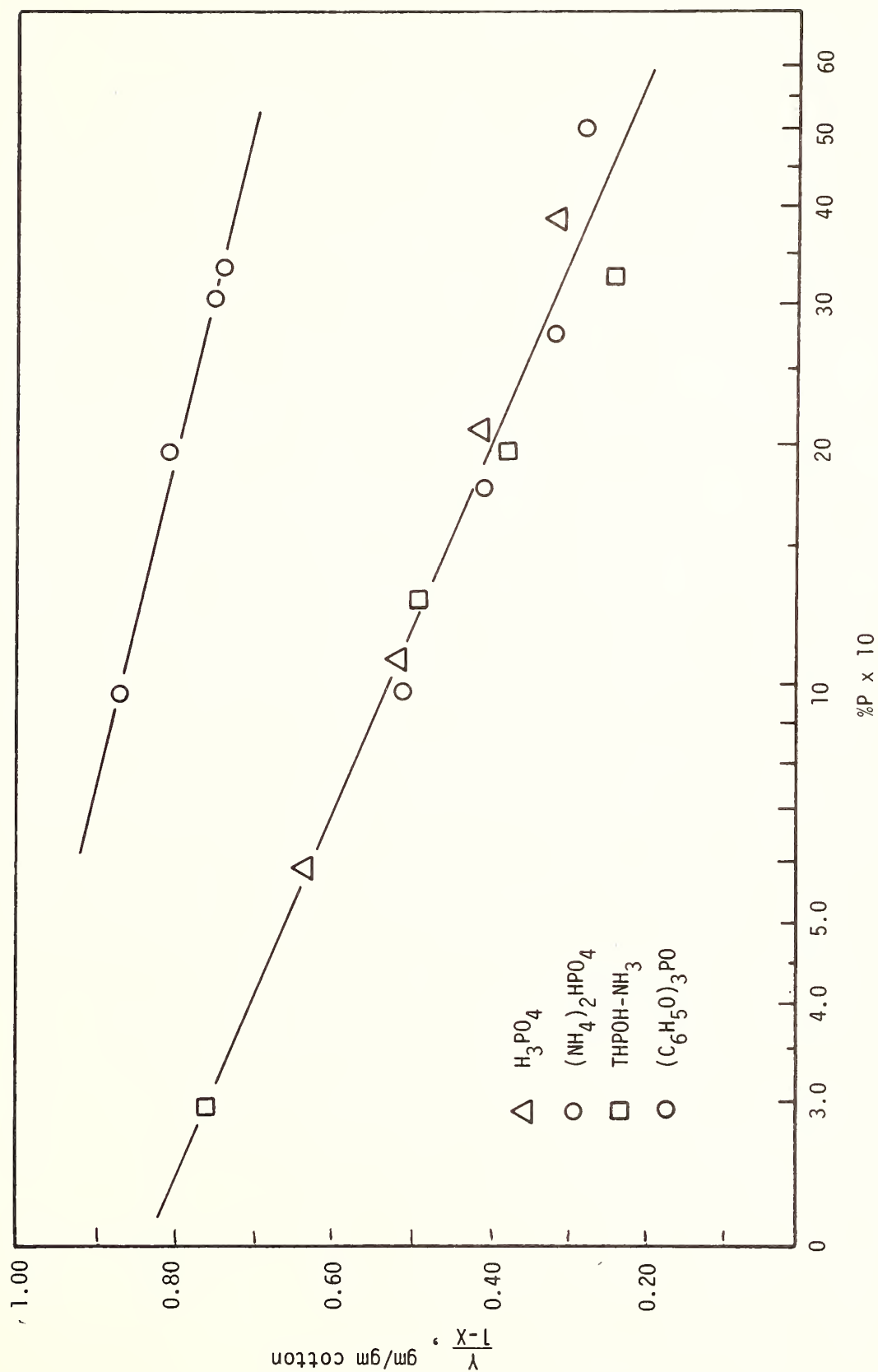


FIGURE 18. Estimated tar formation for treated cotton.

thermally stable systems is therefore given by the effectiveness of the interaction between cellulose and the phosphorus oxides. The only possibility for their efficiency to be enhanced would be for them to be converted into some degradation product other than phosphorus oxides by preceding reactions with an additional reagent applied to the cellulose. This has been found to constitute the basis for the phosphorus-nitrogen synergistic effects observed by many workers (16). In this case, the phosphorus and nitrogen compounds react on heating to form a P-N polymer. The phosphorus atoms in this polymer have considerably enhances reactivity toward the cellulose and are much more efficient as flame retardants. This has been confirmed by model compound studies.

The situation becomes considerably more complex when the flame retardants are thermally stable up to the point of polymer degradation. In such systems the nature of the phosphorus-containing function group is important in determining the flame retardant efficiency of the system. In order to study this effect, compounds of the type $\phi_n P(O\phi)_{3-n}$ and $\phi_n P(O)(O\phi)_{3-n}$ having $n=0, 1, 2$ and 3 have been synthesized and applied to cotton fabric. Calorimetric evaluation of these shows that the efficiency of the flame retardant system increases as the number of oxygen atoms bonded to the phosphorus increases (15) as shown in Figures 19 and 20. An exception to this behavior is observed with triphenylphosphate which probably represents a special case because of its volatility. This would indicate that for thermally stable flame retardant additives the efficiency of the system can be limited by the chemical nature of the phosphorus compound.

Substantiation for this proposal has recently been realized by a study of phosphoramides and related compounds (16, 17). Simple phosphoramides such as $(CH_3NH)_3P=O$ and $(\phi NH)_3P=O$ exhibited efficiency characteristics that were significantly different from those P-O compounds studied earlier. In all cases, the P-N systems were more effective flame retardants. The volatility of the methyl compound was a major factor in determining its effectiveness but this could be altered by various fixation techniques. In these systems there apparently is a competition between volatilization and reaction with the cellulose.

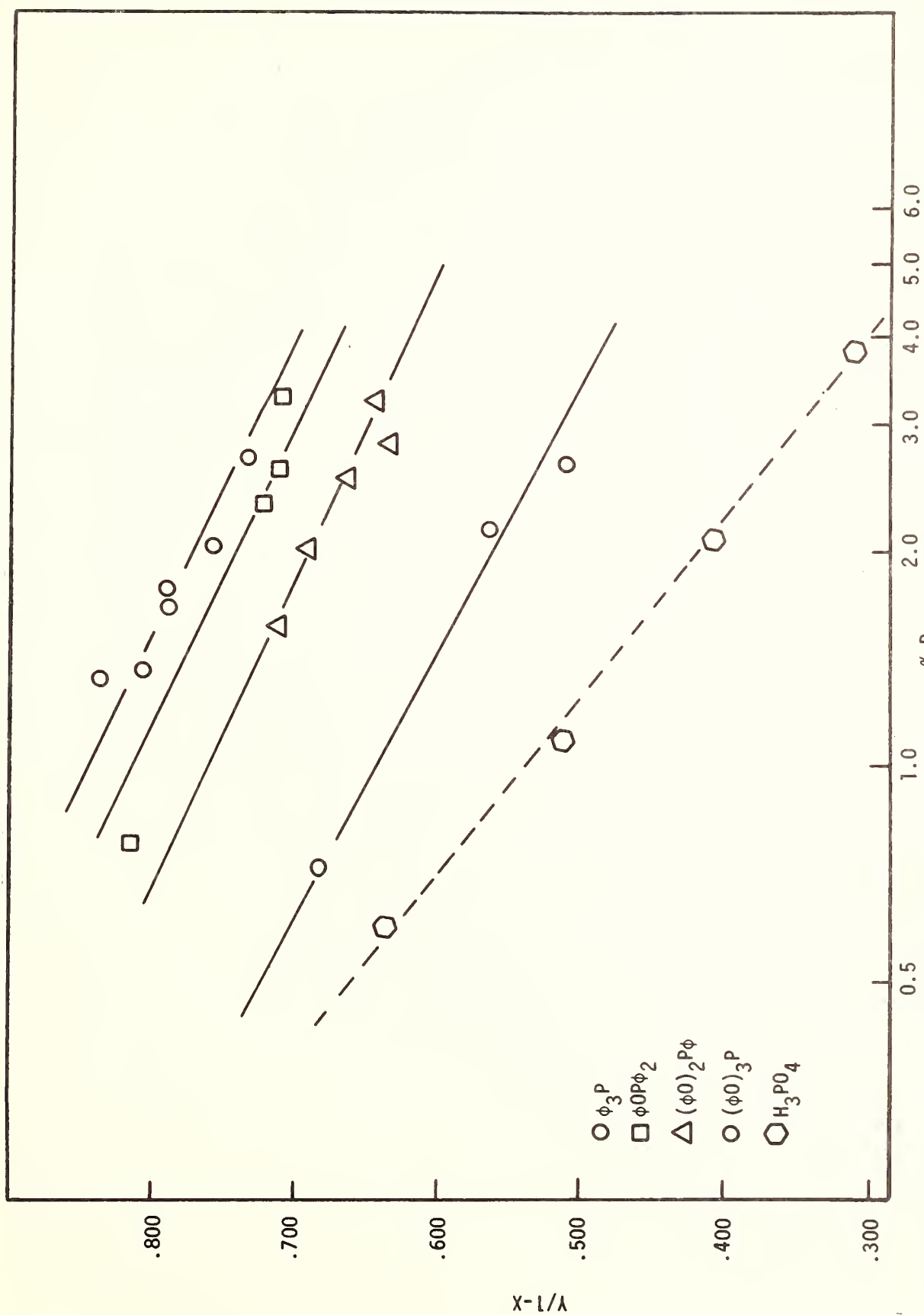


FIGURE 19. Flame retardant efficiencies of trivalent phosphorus compounds.

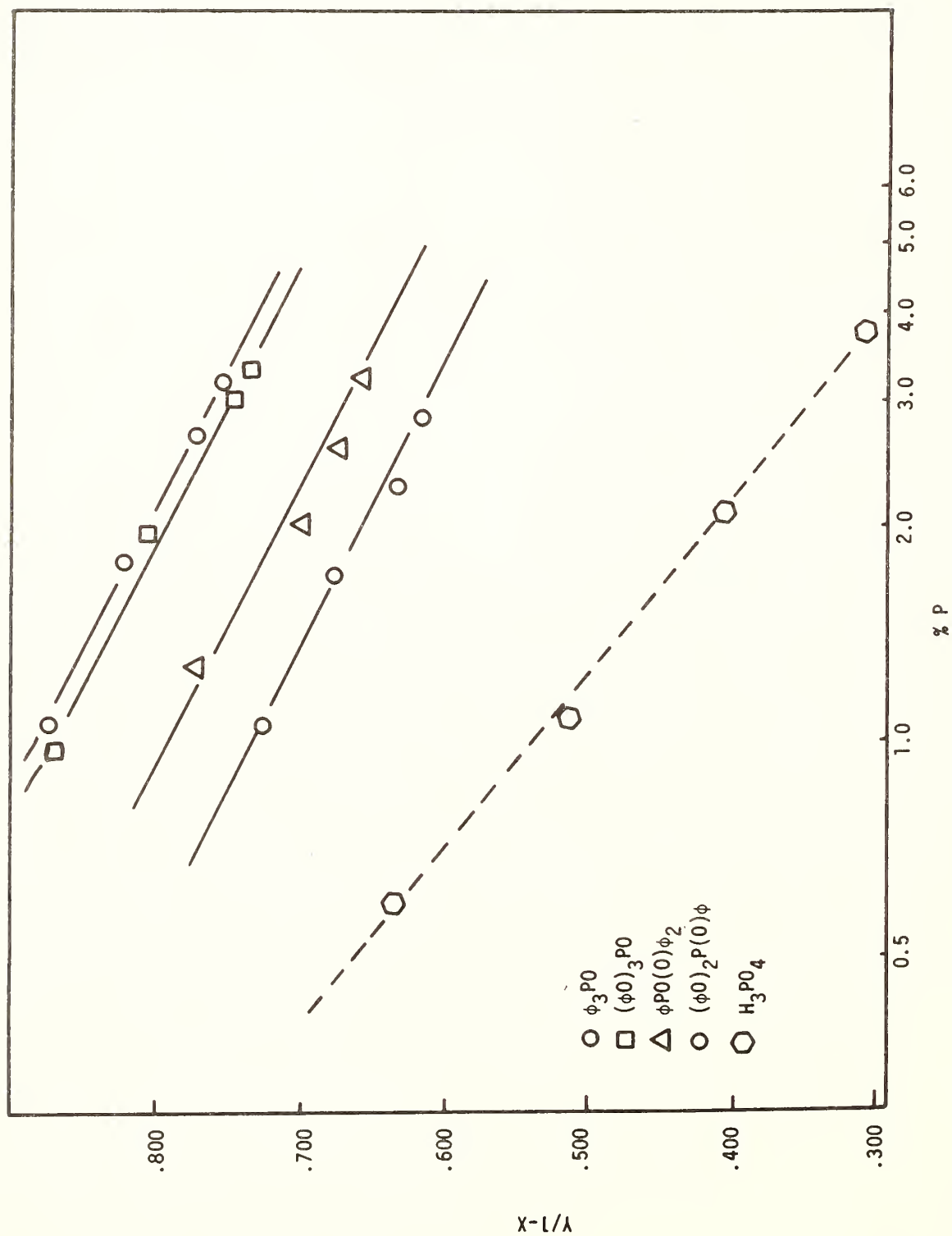


FIGURE 20. Flame Retardant efficiencies of pentavalent phosphorus compounds.

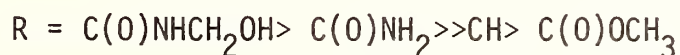
Added evidence of this interpretation is presented by recent results (17) from a study of the efficiencies of a series of model flame retardants of the type $\phi_n P(O)(NH\phi)_{3-n}$ and $(\phi O)_n P(O)(NH\phi)_{3-n}$.

All of these results, when viewed in the context of other experiments involving product analysis and model compound studies (18, 19), allow the postulation of chemical mechanisms to explain the interaction of phosphorus flame retardants with cellulose. The efficiency of such reagents appears to be related to the electron density at the phosphorus atom. As the electron deficiency increases, the molecule becomes more electrophilic and more acidic. This leads to enhances reactivity in phosphorylation reactions and increased its efficiency in catalyzing the degradation of the cellulose. Both of these reactions inhibit the formation of flammable volatiles from the cellulose and promote formation of char and incombustible volatiles.

Although such correlations are fairly straightforward in most cases, the calorimetric technique is also capable of discerning unusual and unexpected effects. For example, it has recently been found that for structures of Type I the flame retardant efficiency of the phosphorus compound is in the order indicated and depends strongly upon the chemical nature of the moiety attached to the other end of the carbon chain (16).



I



The reasons for these unusual structural effects are not obvious from the calorimetric data alone; but these results have been interpreted in terms of an interaction between the phosphorus- and nitrogen-containing groups within the same molecule. This happens prior to interaction with the cellulose so that the species which reacts with the cellulose is most probably a phosphoramidate rather than a phosphonate.

Since the results of applying the calorimetric technique to cellulose were so useful and instructive, an attempt was made to apply the

method to polyester (12). Pure poly(ethylene terephthalate) (PET) fabric under normal atmospheric conditions was found to melt in the igniting flame. This resulted in dripping of the flaming polymer. Collection of the molten material resulted in quenching which did not allow for complete air combustion of the PET. Also a large volume of black smoke was liberated and this was not easily collected for further combustion.

This study also indicated that while PET could not be investigated directly by static oxygen bomb calorimetry, a related polyester, poly-(1,4-cyclohexylene dimethylene terephthalate) (PCHDT) could be studied. The PCHDT has a higher melting point (290°C) which allowed the fabric integrity to be maintained long enough for ignition to be achieved. Since tris(2,3-dibromopropyl)phosphate (TBPP) has been used as a flame retardant on polyester, it was studied along with triphenylphosphate (TPP) to contrast the efficiency of two phosphates as flame retardants, one of which contained halogen. The calorimetric heats of combustion of PCHDT fabric treated with TBPP decreased linearly with increasing amounts of TBPP due to its lower heat of combustion (1841 cal/g). However, with TPP the heats of combustion of treated fabric remained essentially the same since the $(\Delta H_{\text{C}}^{\circ})_{\text{TPP}}$ is 6799 cal/g which is almost the same as that of PCHDT (6878 cal/g). The conditions used in determining these heats of combustion are such that total combustion of all the organic material is achieved.

The situation is much different when the combustion are carried out under atmospheric conditions. Thus, samples of these treated fabrics were burned and weighed. With TPP the char yield increased only slightly as the phosphorus content in the fabric was increased. However, with TBPP there was a significant increase in the residue.

Determination of the heats of combustion of these chars (Figure 21) indicated that the TPP and TBPP chars were quite different thermochemically, and apparently the chemical nature of the char is modified significantly when larger quantities of phosphorus are present. Also, while bromine is generally assumed to operate in the vapor phase when used as a flame retardant, the large differences in the heats of com-

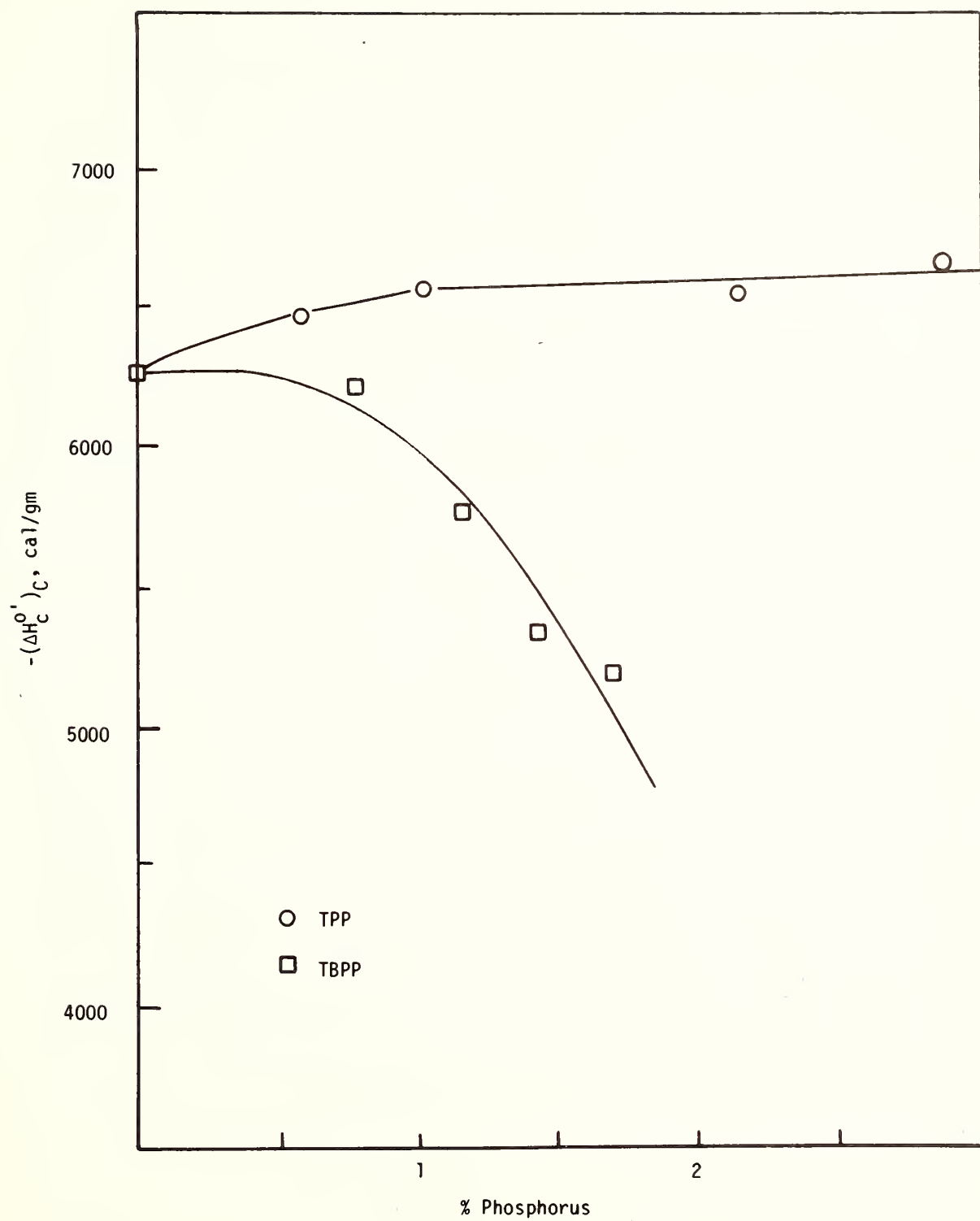


FIGURE 21. Heats of combustion of char.

bustion of the chars suggest that some of the bromine may be effecting the decomposition in the condensed phase (12).

Using these data, corrections can be applied to the heats of combustion obtained for the fabrics and ΔH values corresponding to the heat liberation in the open air can be calculated. These are the values which are expected to parallel the flame retardancy observed for the two treatments. With TBPP the incorporation of increasing amounts of phosphorus into the PCHDT fabric not only reduced the overall heat of combustion, but also increased the char residue to better than 50% at a level of 1.6% phosphorus. At the same time the net heat evolution was reduced from 5073 cal/g with no phosphorus to 3796 cal/g at 0.7% phosphorus and approximately 2100 cal/g at slightly less than 1.7% phosphorus.

In an analogous treatment, the fabric impregnated with TPP exhibited total heats of combustion which are essentially the same with increasing phosphorus content. In this case, the TPP was not effective in increasing the residue formation significantly, and the net heat values only decreased from 4463 cal/g at 0.6% phosphorus to 3805 cal/g at 2.85% phosphorus. Thus, this material would not be expected to exhibit good flame retardant properties.

In an attempt to increase the mechanistic significance of these data, Y values similar to those used in the discussion of the cellulosic were calculated. The data for TPP treated samples (Figure 22) showed decreasing values for Y for increasing phosphorus content. But even with approximately 2.7% phosphorus, the fabric was still decomposing in such a way that about thirty percent of the polyester was being converted into the flammable volatile compounds which serve as fuel for the flame. As was observed with the ΔH_2 values, a linear relationship exists between $Y/(1-X)$, the fraction of polyester converted to flammable gases, and the logarithm of the phosphorus content. As before, the mechanistic significance of the linearity is somewhat ambiguous.

With TBPP, the fraction of treated polyester converted to flammable gases, $Y/(1-X)$, increased more rapidly than with TPP when the

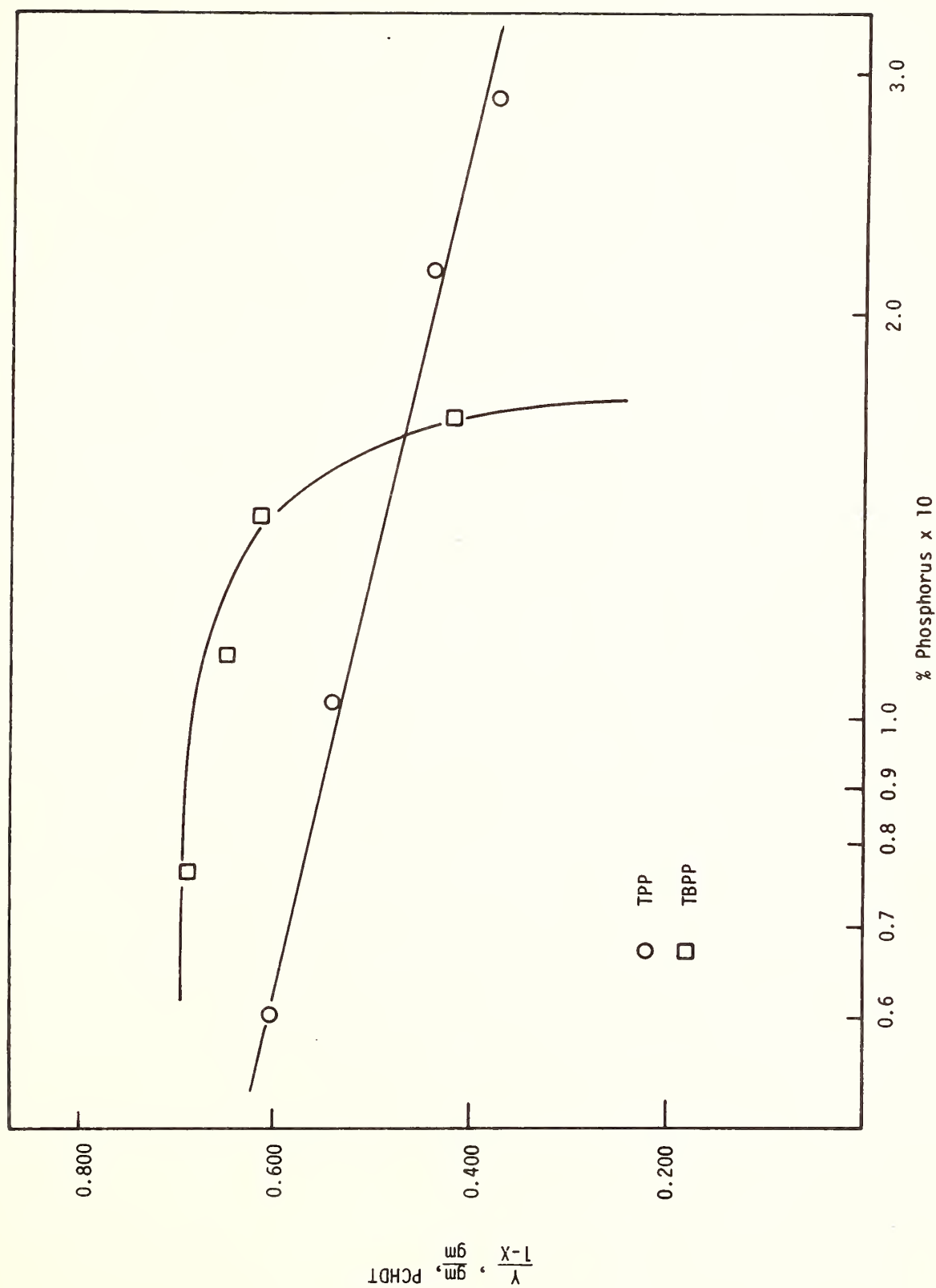


FIGURE 22. Estimated fuel formation for treated PCHDT.

lower levels of phosphorus contents in the fabrics were compared. This indicated that the polyester burns more easily with small amounts of TBPP as a flame retardants, and that in char formation the effects of scaffolding were greater than those of the inhibition reaction at the lower percentages of phosphorus from TBPP. After the TBPP and TPP lines cross, the inhibition reaction dominated, and the TBPP was clearly more efficient than TPP in reducing the fraction of treated polyester converted to flammable gases. Also, these results indicate that using a semi-durable flame retardant finish which could be removed or hydrolyzed to leave a low percentage of phosphorus may create a polyester fabric that could present an increased hazard. This apparently greater hazard which has been indicated thermochemically confirms a visual observation that many investigators have made while conducting actual burn tests.

The further utility of this method has been demonstrated in studies of blends containing polyester (12). It has been established that most synthetic polymers burn rather well when suspended by a carbonaceous grid formed from combustion of cellulosic or other nonmelting materials. If polyester is blended with cotton cellulose, the molten polymer is not permitted to drip away and the combined system is flammable. The calorimetric heats of combustion of cotton cellulose and a series of cotton/polyester blends were measured and are tabulated in Table I. In this case the presence of the nonthermoplastic cotton allowed the combustion experiments to be carried out at the 45° angle so that there was no appreciable amount of material lost from the burning fabric due to melting and dripping. These data show that there is a linear relationship between the percent of cotton and heat liberated. As the cotton cellulose was decreased from 100 percent to twenty percent in a cotton/polyester blend, the heat liberation increased from 3890 cal/g for pure cotton to 4746 cal/g for a fabric containing 80% polyester. This indicated that the combustion of the polyester portion is a significant factor in such blends.

Of course, as previously noted, all of the heats and fuel blends $Y/(1-X)$ obtained for polyesters and the cotton/polyester blends con-

TABLE I

HEAT OF COMBUSTION OF POLYESTER AND COTTON CELLULOSE

Fiber	$-(\Delta H_C^0)_F$ (cal.gm ⁻¹)	R	$-(\Delta H_C^0)_C$ (cal.gm ⁻¹)	$-\Delta H_2$ (cal.gm ⁻¹)
Cotton Cellulose	4013	0.015	7900	3890
Cotton/Polyester*				
87.5/12.5	4145	0.031	6354	3948
75/25	4328	0.039	6216	4086
62.5/37.5	4535	0.045	6919	4224
50/50	4757	0.052	6911	4398
35/65	4907	0.046	7512	4561
20/80	5159	0.066	6264	4746

*Dacron[®] type 54

tained the error introduced by the generation of smoke and other incomplete combustion products. This is inherent in the method because of the assumption of complete combustion in the vapor phase. Thus systems exhibiting heavy smoke production cannot be accurately studied without correcting the equations used in calculating heat release. The ΔH_2 values which are calculated and which serve as the basis for the fuel values $Y/(1-X)$ represent maximum values. To obtain a more accurate set of data it was necessary to devise a method for the direct measurement of the heat release. For this, Yeh and co-workers have devised a technique using an isoperibol calorimeter (20, 21). The calorimeter functions essentially as a heat exchanger, the temperature rise of which is measured using a thermopile attached at several points and referenced to the calorimeter shield. The theory for this type of calorimeter had been worked out previously (22-24).

In practice, a sample of approximately 5 x 12cm., depending upon the size of the calorimeter, is burned while suspended in the calorimeter. Air is pulled through the calorimeter at a rate of approximately 65 liters per minute to obtain maximum combustion in the air. Under these conditions combustion similar to that obtained in the vertical burning used in the static oxygen bomb method is achieved. Char values obtained in the isoperibol calorimeter are very similar to those obtained in open air burning. The temperature-time response of the isoperibol calorimeter is recorded on a strip chart recorder.

The work done on the calorimeter (W) by either a burning fabric or the gas burner used in the calibration experiments is expressed by equation {1}

$$W = E \Delta T_c \quad \{1\}$$

where E is the "energy equivalent" of the calorimeter in cal/mV determined in the calibration experiments and ΔT_c is the corrected temperature rise of the calorimeter. The value of ΔT_c is calculated from the response curve and equation {2}

$$T_c = T_2 - T_1 + b_1 \int_{t_1}^{t_2} (T - T_\infty) dt \quad \{2\}$$

where T , T_1 , T_2 , and T_∞ are the observed temperatures of the calorimeter at the times t , t_1 , t_2 and T_∞ respectively and b_1 is the cooling constant for the calorimeter.

At some time t after the heat source (fabric or calibration burner) has been removed from the calorimeter, the temperature is found to become a single exponential function of time and is described by equation {3}

$$T - T_\infty = a_1 \phi_1 \exp(-b_1 t) \quad \{3\}$$

where a_1 is a function of the initial conditions and ϕ_1 is a geometric factor which depends on the location of the temperature measuring device in the calorimeter.

When the T of the calorimeter is defined by equation {3} then the calorimeter is said to be in a rating period and the change in temperature is given by equation {4}.

$$\frac{dT}{dt} = -b_1 (T - T_\infty) \quad \{4\}$$

The only requirement then is that the calorimeter must reach a rating period before ΔT_c is evaluated. Experimentally Yeh found that the calorimeter entered the final rating period 150 seconds after ignition of a sample (20). The initial rating period at $t=0$, $T=T_0$ is the period before ignition. From equation {4} and the slope of the response curve at two different times during the final rating b_1 and T_∞ calculated. From these data and the value of the integral in equation {2} from $t=0$ up to $t \geq 150$ sec. T_c is calculated. The total heat release is then obtained from expression {1}.

The value of E is determined in calibration experiments in which known amounts of propane are combusted in the calorimeter. In his calibration experiments Yeh (20) observed a precision of $\pm 3\%$. However, he estimated that the overall accuracy of the calorimeter was really about $\pm 7\%$, due to various systematic errors such as radiant energy loss from the bottom of the calorimeter and incomplete cooling of the exhaust gases. The rate of burning is measured from the slope of the response curve. In the work of Yeh and co-workers a least-squares re-

gression of the data yielded the expression:

$$\text{Rate} = Q = 236.6S$$

where S is the slope of the line in mV/sec. The standard deviation of the slope in their work was 5% with an estimated accuracy of 10%.

Comparisons of the heat release values measured in the isoperibol calorimeter with those determined by the static oxygen bomb method were made. The oxygen bomb heats were higher. This is not unexpected since ΔH_2 represents the maximum possible heat release which would be obtained only with the total combustion of all volatized materials. Except in those cases where the melt-drip properties of the fabrics made it impossible to collect residues representative of the fabric's ability to form chars $\Delta H_1/\Delta H_2$ was found to be in the range of 80-90%. Cotton showed the largest percentage heat release indicating the validity of using the oxygen bomb calorimetry method for lightweight cotton fabrics.

To extend this, Yeh has used isoperibol calorimetry to measure heat release and rates of burning of cotton fabrics treated with some of the same model flame retardants used in the earlier oxygen bomb experiments (21). As part of this experimental set-up, a combustible gas detector was attached to the exhaust of the calorimeter. This allowed the measurement of the heat contents of the uncombusted gases. From these data he was able to show that $\Delta H_1 + \Delta H_3 = \Delta H_2$. Thus, the explanation that $\Delta H_2 < \Delta H_1$ due to incomplete combustion was verified by experiment. This also allows one to use this difference as a probe into the vapor phase behavior of these systems.

Yeh also compared his isoperibol heat values with the ΔH_2 values obtained earlier (21). In all cases ΔH_1 was found to exhibit the same trends as ΔH_2 . In addition, on the basis of heat values, the results gave a similar evaluation of the flame retardant efficiencies of the three retardants (diammonium phosphate > phosphoric acid > THPOH-ammonia). In each case, however, the actual differences among the 3 were quite small. Of particular significance are the ratios $\Delta H_1/\Delta H_2$ and $\Delta H_3/\Delta H_1$. The fraction of heat released or the fraction of complete combustion in the gaseous phase is reflected in $\Delta H_1/\Delta H_2$. Within each

of the treated systems the fraction of heat released is essentially constant and independent of the flame retardant add-on. This is of significance not only in determining the completeness of combustion but also in establishing the mechanism of flame retardant action (21). Since the presence of the flame retardant does not seem to affect the completeness of the combustion of the volatilized materials, it can be assumed that the locus of action of all three retardants is predominantly in the condensed phase. This is in agreement with the results of other studies using other techniques. Although it has not yet been done, it would seem on this basis that the comparison of calorimetric values offers a powerful tool for the study of flame retardants and their location of action. It should be of particular interest in the study of those retardants presumed to be active in the vapor phase.

The rates of heat release also constitute an important characteristic of flame retardant fabrics. These are easily obtained by the isoperibol technique. This is shown by the results of the work of Yeh and co-workers (21). An identical dependence of rate of phosphorus content was observed for all three systems and interpreted in terms of considerable mechanistic significance. The fuel values $Y/(1-X)$ for all three treated systems had previously shown an identical dependence on the phosphorus content. Thus it was concluded that these three retardants operate through the same mechanism. Isoperibol calorimetry confirms this. A direct correlation of this theoretical fuel yield with the rate of heat release was found. This correlation would seem to indicate that this is somewhat reflecting the kinetics of cellulose pyrolysis. However, due to the ambiguity of the heterogeneous kinetics involved, exact interpretation could not be made.

A correlation was also found to exist between the isoperibol rates of heat evolution and the rates of flame propagation measured earlier by Hendrix et al. On the basis of the relationship

$$\dot{Q}/Y = -\Delta H \delta \dot{x}$$

Yeh and his co-workers were able to interpret these results. In this expression \dot{Q}/Y gives the rate of heat release in cal/sec cm., $-\Delta H$ is the heat release in cal/g, δ is the fabric weight, and \dot{x} is the burning

rate in cm/sec. It is obvious from this that the linearity can only be followed up to a small range of retardant add-ons where incorporation of the retardant into the fabric does not significantly alter δ . However, the fact that this equation holds for untreated cotton as well as that treated with the model flame retardants was interpreted as indicating that the products of pyrolysis are not significantly altered by the presence of the retardants in the fabric. The action of the retardants is to alter the amount of fuel. This would be in agreement with the earlier results of Hofmann and Raschdorf (25). Their work showed that the major gaseous products from the combustion of untreated cottons were the same as those from samples containing phosphorus flame retardants. Only the quantities of fuel were reduced. They also concluded that the primary action of phosphorus and nitrogen containing retardants was as a catalyst for the thermolysis of the cellulose. Of perhaps greater significance, Yeh has pointed out that ΔH_1 calculated from the slope of the fitted curve relating isoperibol rates and flame propagation rates has a value of 3620 cal/g, which is very close to 3688, the known heat of combustion of cellulose.

This isoperibol calorimetric method has also been shown to provide some valuable insight into the flammability of blends and the effects of various types of flame retardants. In one particularly interesting study, Yeh and co-workers (8) investigated a series of blends with various blend levels in which the cotton had been impregnated with H_3PO_4 . Earlier work (9) had shown that this material exerts its retardant effect in the condensed phase by changing the rate and mode of pyrolysis of the cellulose and increasing its char production. Examination of the fabrics by isoperibol calorimetry led to the results shown in Figure 23. As can be seen, the response to this treatment of high cotton blends was vastly different from that of the high polyester blends. In this first case, increasing amounts of retardant significantly reduce the heat output from the burning fabric; but in the second case, increasing amounts of retardant produce a small, deleterious effect. The nature and origin of this effect is not understood at present, but presumably a similar effect could exist with

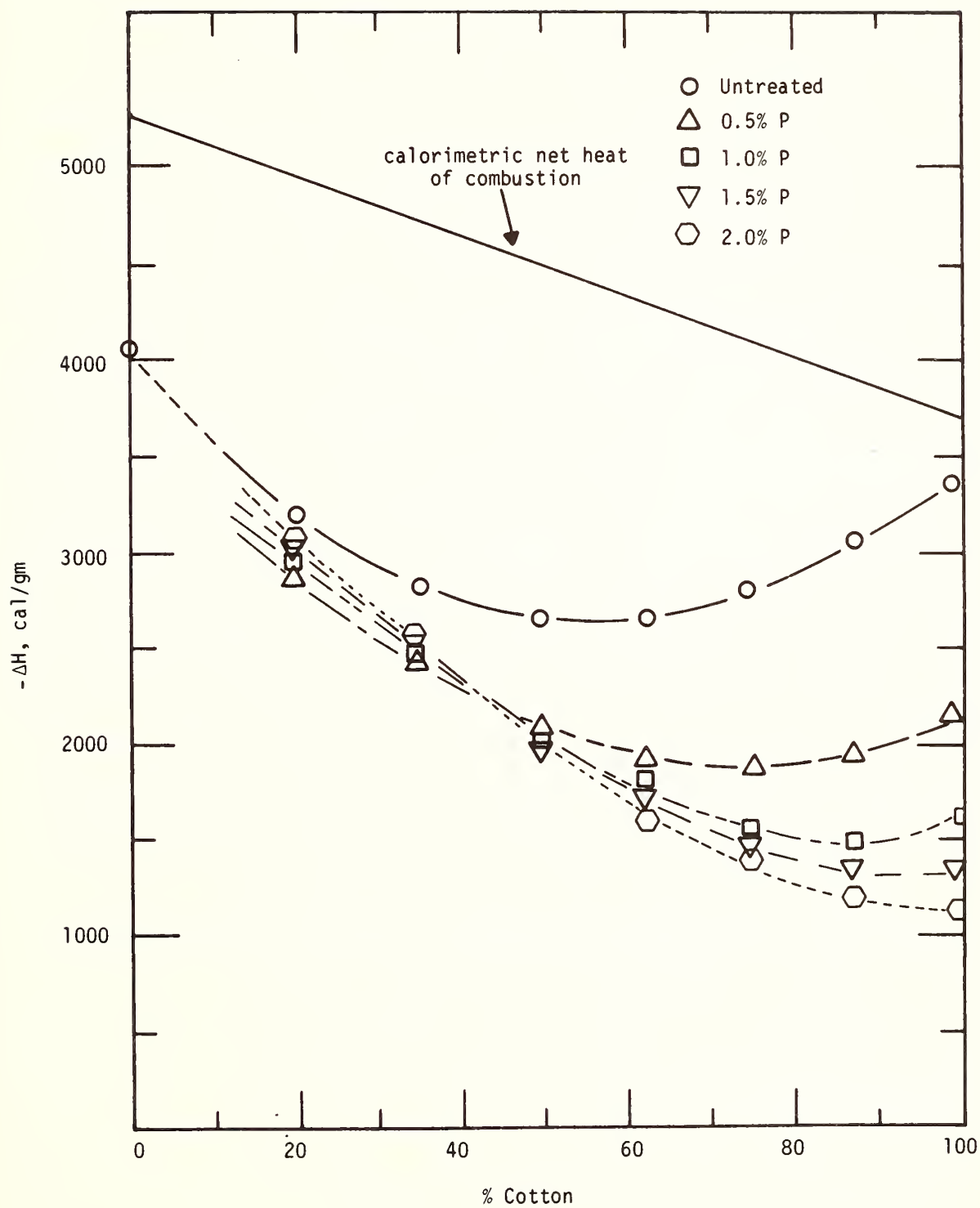
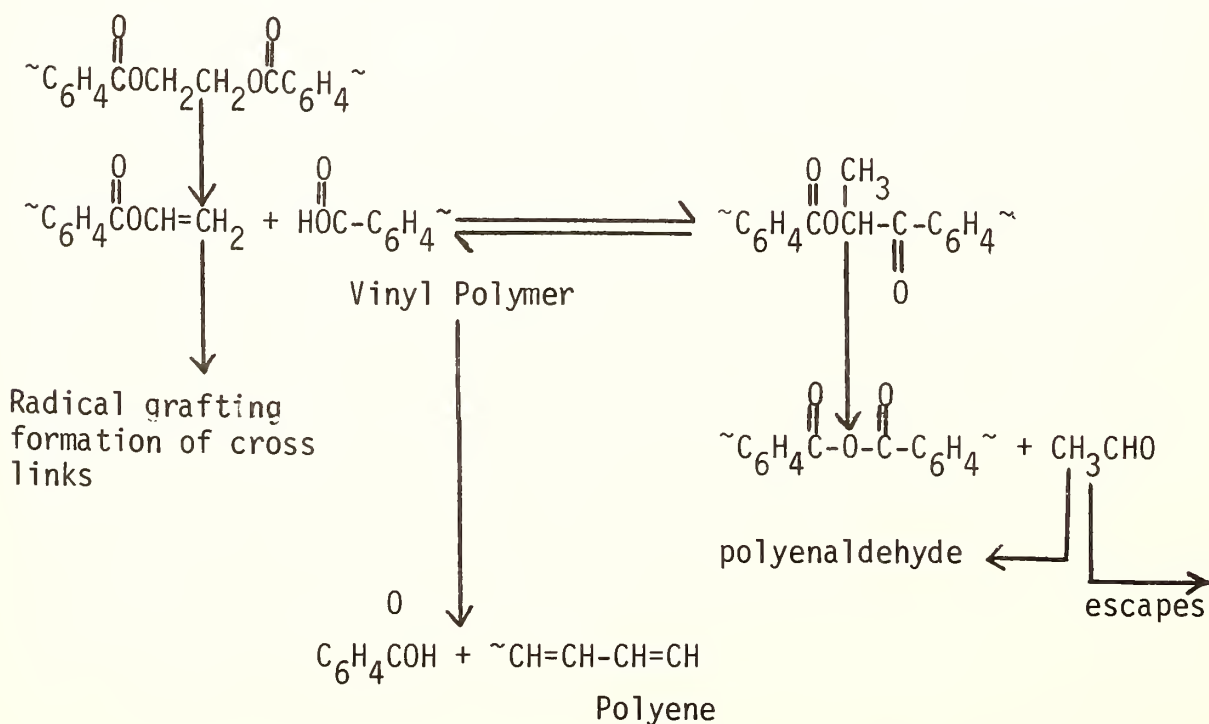


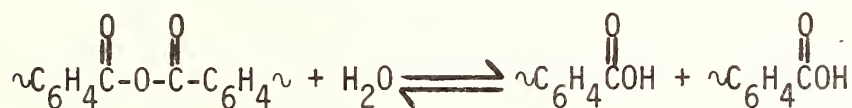
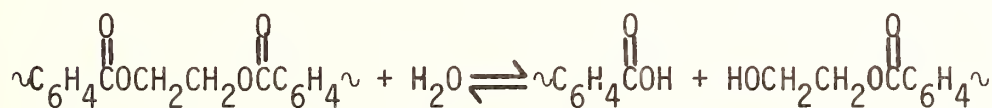
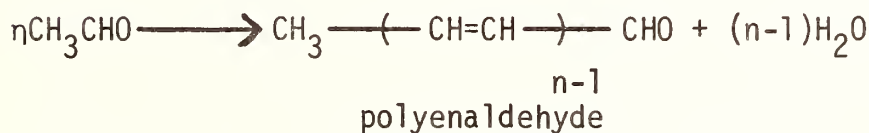
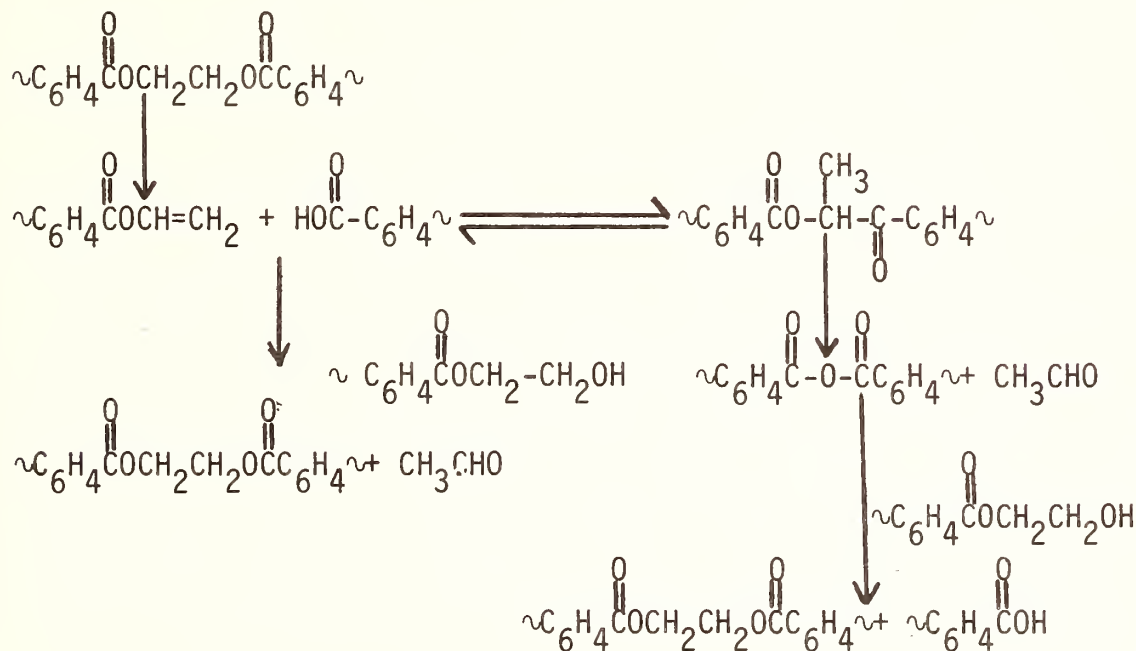
FIGURE 23. Treated heat releases of H_3PO_4 PET/cotton blend fabrics.

blends having only the polyester portion treated.

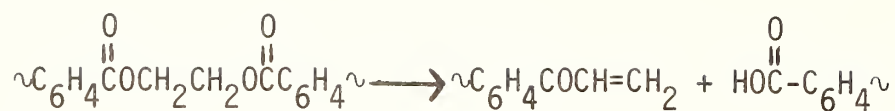
Unfortunately, the calorimetric techniques which have proven to be such powerful mechanistic probes for cellulose have not been widely applied to thermoplastics. Thus much less is known about the action of flame retardants in polyester than in cellulose. To date, the only really significant advances in this area relate to the understanding of the reactions responsible to the production of flammable gases from thermalyzing polyester. A number of simple esters have been studied as models for poly(ethylene terephthalate). From these a number of the features of the polyester degradation have been determined. The thermal degradation of polyester itself has also been studied by several investigators (26-31) in recent years. Although Marshall and Todd (31) proposed that the rupture of a C-O bond during the thermal degradation of PET would produce resonance stabilized radicals, none of the other investigators have found evidence to substantiate such a free radical mechanism. PET decomposes by random chain scission at the ester links (A^1 scission), and the principal point of weakness in the polyester chain appears to be the beta-methylene group (32). The major thermal degradation reactions of PET are summarized as follows: (26-28)



This mechanism is very similar to the mechanisms proposed for the pyrolysis of ethylene dibenzoate and vinyl benzoate. If 2-hydroxyethyl end groups are considered, the following reaction mechanism for the decomposition of PET is proposed (28):



Thus, as long as free hydroxyl end groups exist in the PET melt, the broken polymer chains will be reformed with production of an equivalent number of acetaldehyde molecules and carbonyl end groups. The molecular weight of the polymer will begin to decrease when most of the hydroxyl groups have been consumed. The detailed mechanism of the conversion of a PET unit, i.e.



is as yet only speculative, although the close agreement between the decomposition of poly(ethylene terephthalate) and ethylene dibenzoate suggests that it is probably similar to the mechanism for simple ester pyrolysis (28).

When molten poly(ethylene terephthalate) is maintained under nitrogen at ca. 280°C, the polymer decomposes with (a) evolution of gas, (b) the formation of low molecular weight products of varying degrees of volatility, (c) the formation of different functional groupings in the polymer, and (d) the discoloration of the polymer. The following gaseous products (concentration in mole-percent) are formed (28): CH₃CHO, 79.5; CO₂, 8.5; CO, 8.0; C₂H₄, 2.0; H₂O, 0.8; CH₄, 0.4; C₆H₆, 0.4; 2-methyldioxolane, 0.4. The 2-methyldioxolane arises from the interaction of acetaldehyde and ethylene glycol. Although the concentration of acetaldehyde varies greatly with the temperature of decomposition, it is always the major decomposition product.

The major nongaseous degradation products are terephthalic acid and acidic oligomers (26, 28). An equilibrium seems to exist between the polymer and the cyclic oligomers (mainly the trimer) formed during the thermal degradation. Although the mechanism of oligomer formation is unknown, it is assumed to be transesterification involving end groups. A number of compounds, mainly derivatives of substituted benzoic acids and diphenyldi- and monocarboxylic acids, have been isolated (28) but these were found in very low concentration (0.005 - 0.09 weight %).

Wall (23, 34) has studied the rate of volatilization of PET to determine the mechanism of degradation. Theoretically, random degradation of linear chains is characterized by a maximum in the rate of volatilization which occurs at 26% conversion to volatile products (35). Poly(ethylene terephthalate) (33) fits the theoretical curves for random degradation except that the maximum is at a lower conversion and the volatilization tends to cease at about 80% conversion. The rate

of volatilization at the maximum $(dc/dt)_{\max}$, is independent of the molecular weight of the polymer and is controlled by the expression $(dc/dt)_{\max} = \frac{kL}{2.7}$ where k is the rate constant for rupture of the chain bonds and is related to α , the fraction of bonds broken at the time t , by the relationship $\alpha = 1 - e^{-kt}$ (35). The quantity L is the number of basic units in the smallest chain that does not evaporate without degradation. For PET, $L=5$ in the temperature range studied. These results are consistent with Goodings (28) and Buxbaum's (26) findings of acidic oligomers in the nongaseous products.

As thermal degradation proceeds, the concentration of hydroxyl groups in the polymer decreases and the concentration of carboxyl groups increases. Anhydride groups are formed by the reaction of carboxyl groups with vinyl end groups and by dehydration between two carboxyl groups (28). The concentration of anhydride groups begins to increase when most of the hydroxyl end groups have been consumed. Goodings (28) found that PET which had been degraded for 65 hours under nitrogen at 306°C gave an IR spectrum which indicated that anhydride and carboxyl groups were present in the ratio 1:2:6.

The color of PET changes from white, to yellow, to brown, and finally to black as the polymer degrades thermally. Pohl (29) reported on the basis of selective solubility that the chromophore was chemically bonded to the polymer chain. The chromophore is reported to be a highly unsaturated aliphatic molecule with a molecular weight of about 300-1000 (26, 28). Goodings (28) assumed that the route leading to color formation in PET was the formation of polyenealdehydes from acetaldehyde. Zimmerman, (30, 36) on the other hand, has shown that unsaturated colorforming molecules are produced from poly(vinyl esters). Buxbaum (32) reports that both reactions contribute to color formation with the polymerization conditions determining the predominant reaction sequence.

Investigations of the decomposition reaction kinetics of simple esters (37-39) have shown that the reactions are homogeneous, follow first order kinetics in both the vapor and liquid phases, and are unaffected by radical scavengers. On a theoretical basis, pure chain

scission of the ester link (A^1 scission) would require an activation energy of ca. 60 kcal/mole. Since an activation energy of ca. 40 kcal/mole was found for simple ester pyrolysis, this lower observed value indicates a mechanism probably involving a cyclic transition state.

The rate of thermal degradation of PET can be measured in terms of: (a) the products formed, (b) the rate of change of molecular weight of the polymer (as measured by the intrinsic viscosity or melt viscosity), or (c) the rate of change in the concentration of end groups (32). The reaction rate constants and activation energies found by the various investigators using one or more of the methods mentioned above are shown in Table II. It is significant that all the rate constants have the same order of magnitude. Thus, even though the pyrolysis reactions of PET have not been completely characterized, enough is known about them to make several predictions. For example, it would seem that acidic materials would enhance the thermolysis process and produce increased quantities of acetaldehyde, a combustible gas. Further speculation can also be made concerning the low probability of finding chemical flame retardants which would exhibit conventional types of condensed phase activity.

This latter speculation has been borne out in the one published case in which a polyester flame retardant system was subjected to a thorough mechanistic study (12, 40, 41). In this work an investigation was made of the effects of triphenylphosphine oxide (TPPO) on the thermal decomposition and combustion of polyester. Differential thermal analysis and thermogravimetric analysis were used to monitor the thermolysis reactions. It was expected that phosphorus-containing flame retardant additives would exert their effects by alteration of the condensed phase pyrolysis reactions. The additives originally chosen were nylon 6 and TPPO. Prior laboratory flame tests had shown clearly that the PET/TPPO/nylon system was the most effective in imparting flame resistance (42). The results of thermal analysis indicated very positively that TPPO did not operate as a flame retardant in the condensed phase since the main decomposition of PET was not affected by increasing the amount of TPPO present. These results im-

TABLE II

Reaction Rate Constants and Activation Energies of the Thermal Degradation of PET

K and E_a Calculated From	$K \text{ (h}^{-1} \cdot 10^3) \text{ at } 282^\circ\text{C}$			$E_a \text{ (kcal/mole)}$	
{n} {a}	1.3	2.3	1.4	62.3	--
M. V. {b}	1.7	(290°C)	---	---	32.0
Total Gas	---	---	---	---	38
-COOH	3.5	---	---	41.7	---
-OH	2.4	---	---	---	---
-CHO	0.2	---	---	---	---
Total End Groups	1.2	---	---	58.7	---
{a} Intrinsic viscosity					
{b} Melt viscosity					

plied that any effect exerted by TPPO must be exerted in the vapor phase.

In order to substantiate this, oxygen and nitrous oxide indices were used as previously mentioned. A comparison of OI and NOI for the PET/nylon 6 system showed parallel lines. This indicated that any inhibition effects caused by the inclusion of nylon in the polyester occurred in the condensed phase. The OI and NOI lines for PET/TPPO and PET/TPPO/nylon were divergent. This intimated that TPPO poisoned the flame reactions (vapor phase) since there was inhibition in oxygen but not in nitrous oxide.

Phosphorus analyses of the modified polyester samples indicated the reason for the lower flammability of the PET/TPPO/nylon 6 system. These analyses showed that whenever nylon was present in the polymer, an increased amount of phosphorus was held in the sample. Consequently, the nylon increased the TPPO physically held in the polyester and slowed its sublimation. This has been confirmed in a recent mass spectrometric investigation (41).

The observation has been made that a large amount of energy delivered over an extended period of time will not propagate a flame while the same amount of energy delivered instantaneously will successfully propagate the flame, due to a rapid rise in the temperature. This observation suggested that the hazard due to flammable fabrics is related to both the total amount of heat released and the rate of heat release.

An isoperibol calorimeter was used to obtain the total heat released. These studies suggested that the PET/TPPO system should exhibit the best flame retardancy properties because of the rapid decrease in the heats evolved. But a study of the flammability of these systems using the match test had shown that the PET/TPPO/nylon 6 system was the superior flame retardant system. These results indicated that in vapor phase flame retardant systems the total heat released must be considered along with the other experimental data such as the flammability test results.

This apparent discrepancy was resolved when the rate of heat re-

lease was considered. These results showed clearly that the ternary system had the lowest rate of heat release. These data suggested that for vapor phase active additives the rate of heat release was a more important parameter for determining flammability than the total heat released during combustion. Because of the nature of the flame retardant activity, these conclusions should be as valid for cotton/polyester as they are for 100% polyester.

Although very little mechanistic data is available concerning cotton/polyester blends, it appears that this is actually the case. Most of the flame retardant systems which show effectiveness on blends seem to act on cellulose in the condensed phase and polyester in the vapor phase. None of the studies to date have demonstrated this unequivocally; but all of the data are compatible with such an interpretation. For example, Loss, Hofmann and Nachbur (43) have compared the action of a phosphonate and a phosphonium compound on cotton and blend fabrics. They found that both compounds had lower efficiencies on 65/35 polyester/cotton than on 100% cotton but the relative efficiencies were different (Figure 24). The phosphonate exhibited higher efficiency than the phosphonium compound on 100% cotton whereas the reverse was found in the case of the blend. Although these workers did not attempt to explain their results, it seems likely that the phosphonate is more effective in reacting with the cellulose to provide condensed phase retardancy. Similarly, the phosphonium salt should react more slowly with the cellulose thus allowing some of the material to volatilize and provide some vapor phase activity. Of course, this latter mode of action would be particularly important when the fabric contained significant portions of polyester.

Similar conclusions can be reached on the basis of studies using phosphonates and phosphine oxides. Tesoro (44) has used oxygen index measurements to compare the activity of $(\text{CH}_3\text{O})_2\text{P}(\text{O})\text{CH}_2\text{C}(\text{O})\text{NHCH}_2\text{OH}$ and $(\text{CH}_3)_3\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{NHCH}_2\text{OH}$ on 100% cotton and cotton/polyester blends. In her studies the retardants were applied to the fabrics along with melamine resins and fixed by a pad-dry-cure process. Under these conditions she found the phosphine oxide to have considerably greater

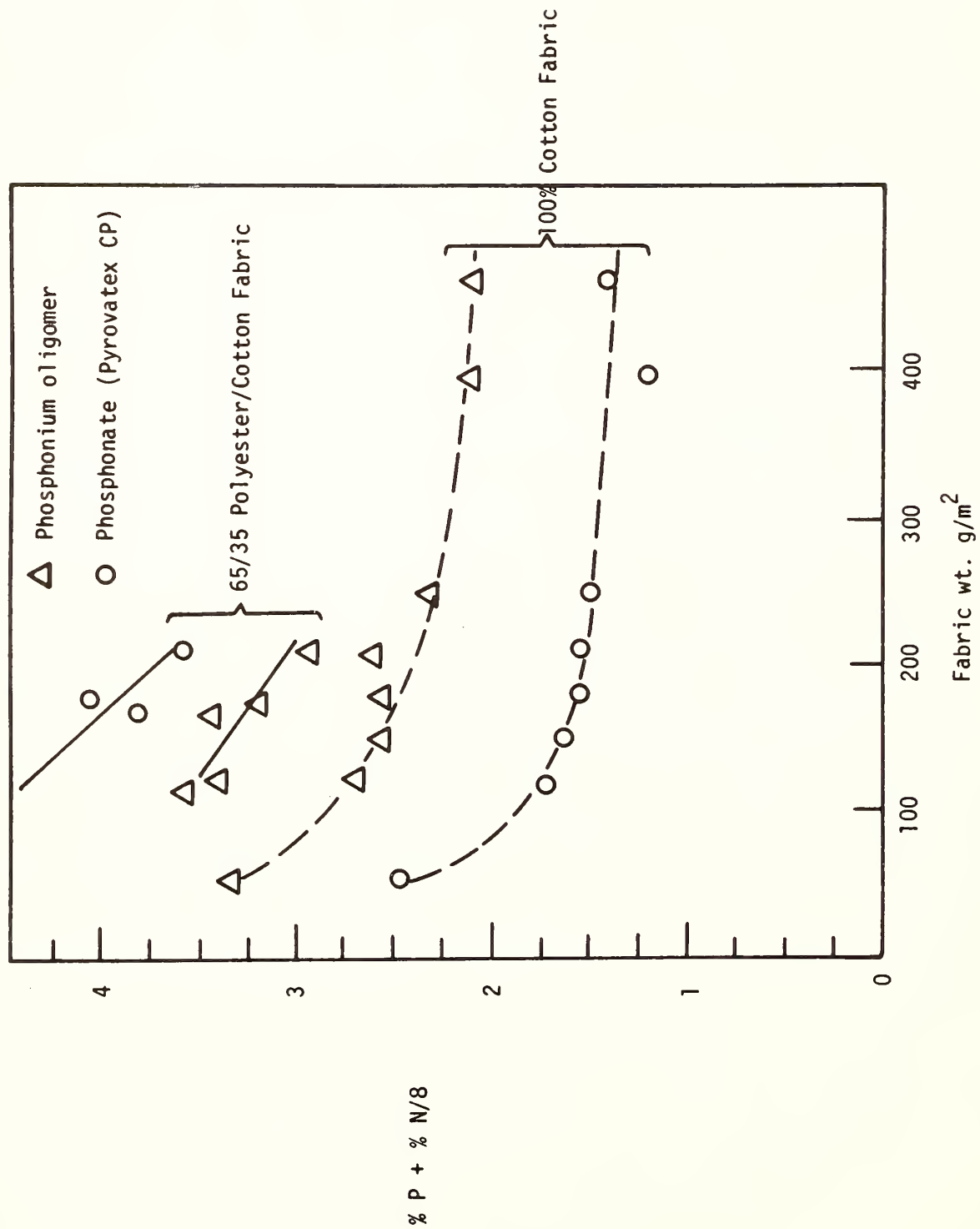


FIGURE 24. Minimum FR content for self extinguishment in vertical test.

effectiveness in both 65/35 (Figure 25) and 50/50 (Figure 26) blends. The reasons for this become clear from her findings that the efficiency of the phosphine oxide was the same on both 100% cotton and the 50/50 blend whereas that of the phosphonate was much lower on the blend than on the 100% cotton. The fact that the phosphine oxide was essentially substrate-independent is indicative of vapor phase activity while the finding that the efficiency of the phosphonate was directly related to the chemical nature of the substrate is strong evidence for condensed phase activity.

Similar results had begun to accrue from an investigation which was in progress at Clemson University (45). The efficiencies of triphenylphosphine oxide and $(\text{CH}_3\text{O})_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{NHCH}_2\text{OH}$ were evaluated. It was found that the phosphonate had essentially the same effect regardless of whether or not it was chemically fixed in 100% cotton fabrics. However, with polyester/cotton blends the situation is quite different. Apparently the reactivity of the phosphonate toward cellulose is high enough to prevent its loss by volatilization when it is present in low concentration; but when it is overloaded as it would be in the cotton portion of a 50/50 or 65/35 blend some volatilization may occur. This could provide some vapor active species to retard the polyester portion and account for the higher efficiency of the unfixed retardant on the blends. In support of this interpretation, a large difference was found in the effectiveness of the phosphonate and triphenylphosphine oxide on 100% cotton fabric. But the two retardants seem to be almost equally effective on 65/35 blends. There was good reason to believe that the triphenylphosphine oxide exerts essentially all of its effect in the vapor phase. These results were therefore interpreted as demonstrating the importance of volatility of the flame retardants when polyester is included in the fabrics.

2. Development of Potentially Commercial Flame Retardants

Although the theory of flame retardant action on polyester/cotton blends had not been elucidated, a number of partially successful treatments were developed by a completely empirical approach. Most of

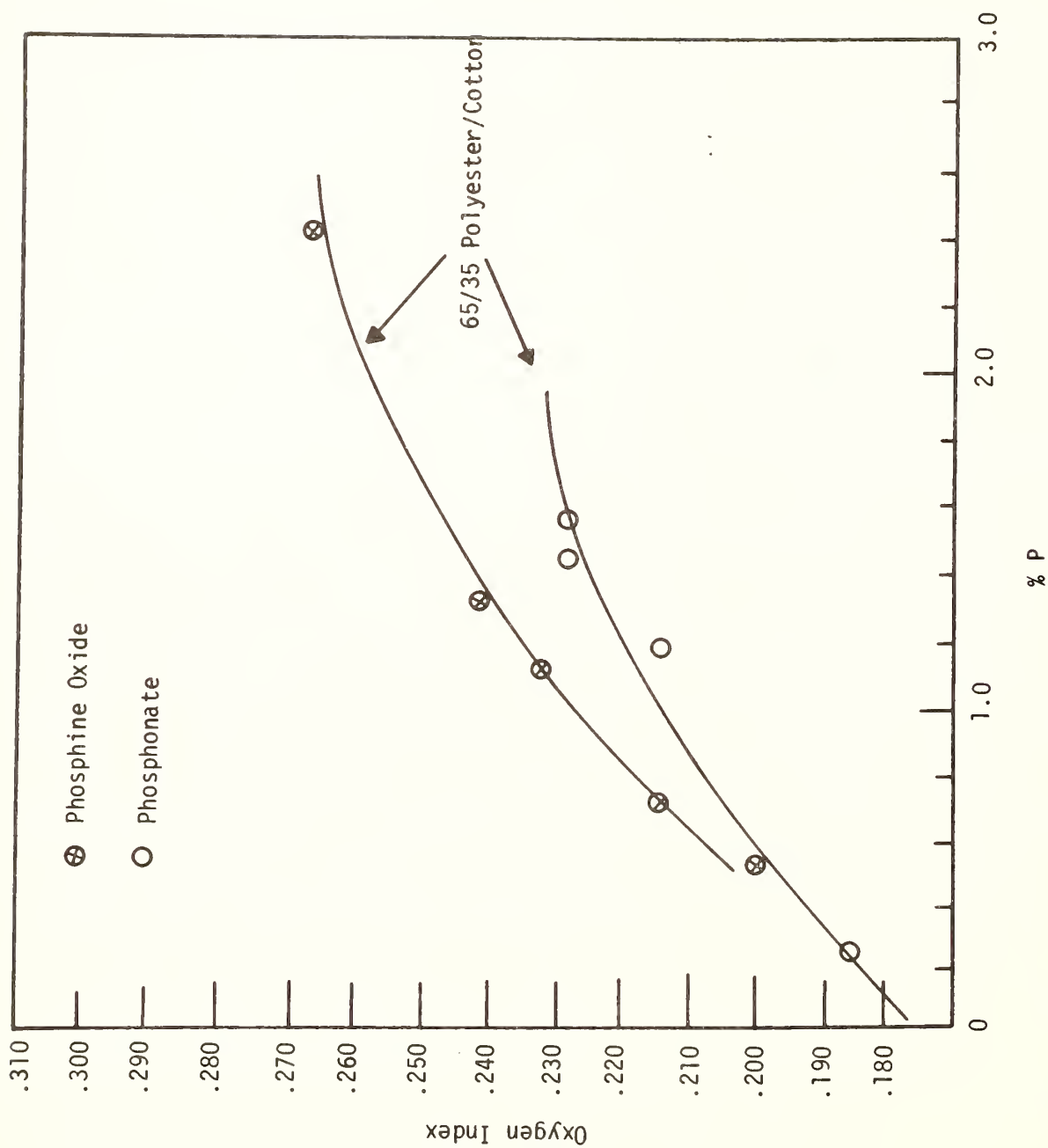


FIGURE 25. Effect of phosphorus flame retardants on the OI of 65/35 PET/cotton blends.

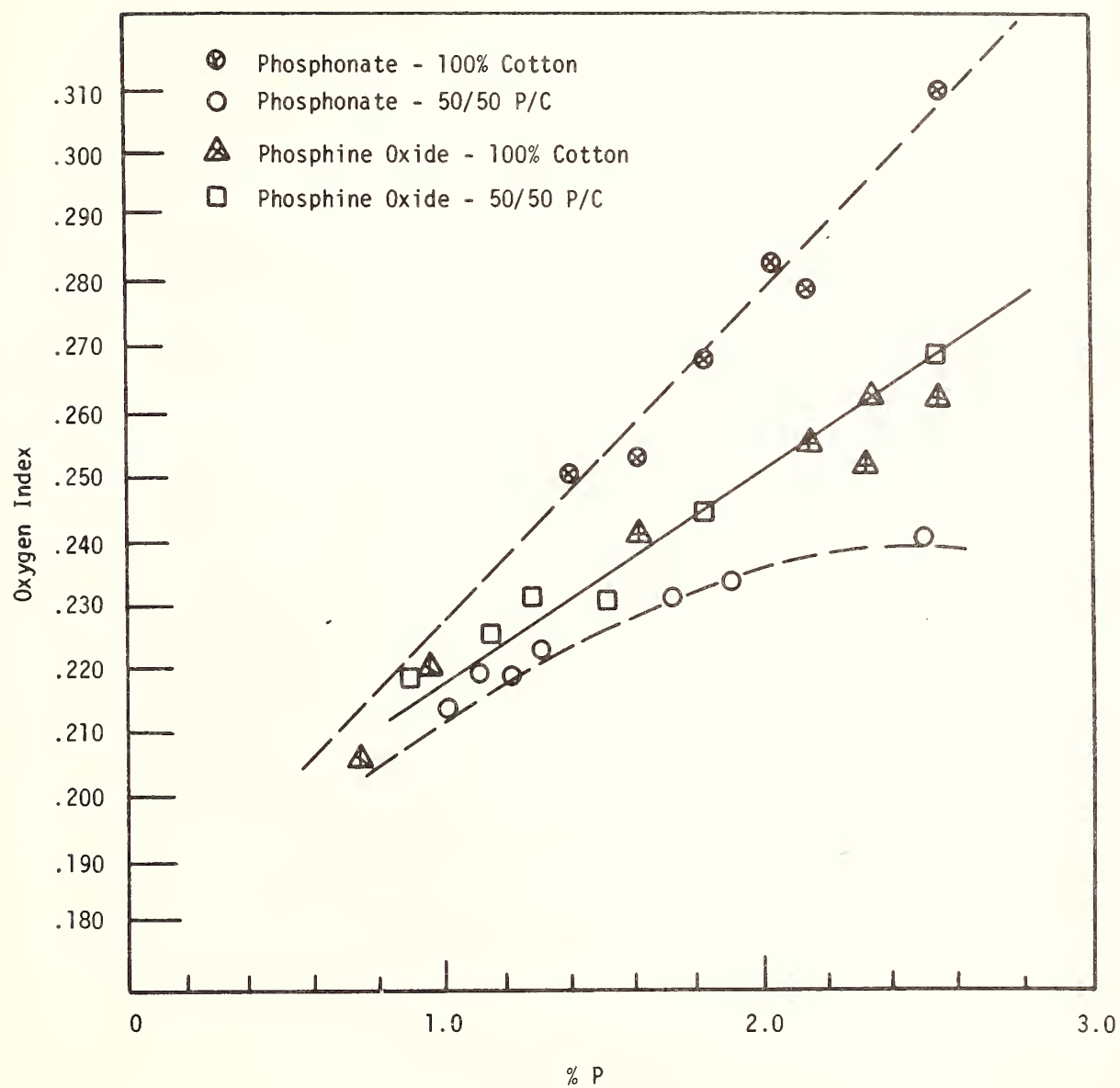


FIGURE 26. Effect of phosphorus flame retardants on the OI of 50/50 PET/cotton blends.

these had rather severe deficiencies, but they could serve as good prototypes for further studies and were informative subjects for theoretical examinations. There are two general methods for obtaining flame-resistant polyester/cotton blend products.

2.a. Blending Fire Resistant Fibers:

This approach is more long range than the other alternatives but it offers some special advantages as well as disadvantages. The flame retardants used in rendering the fibers inherently flame resistant should be the most efficient since they can be specifically designed for each individual polymer. Also, since the modifications are made prior to spinning in most cases there is greater opportunity to maximize the durability of the retardant and minimize the undesirable effects of physical properties of the fibers. On the other hand, such specialty fibers frequently pose significant problems in such areas as cost and inventory management.

The production of such fibers can presumably be achieved by several routes such as copolymerization or grafting with flame retardant monomers or the inclusion of unreactive flame retardants in the spinning melt or solution. Copolymers containing flame retardant comonomers should be easily attained for polyesters as attested by the numerous instances of their use in polyester resins (46). However, the reason that these techniques are not readily applicable to fiber manufacture is basic. Polyester is a linear polymer which must be highly oriented after spinning. It is the basic morphology of these polymers that give the fibers the properties which have made them commercially acceptable. The presence of foreign segments in the polymer backbone tends to disrupt the desired morphology, often to such an extent that the fiber attained has completely different and less desirable properties. Several comonomers also introduce unwanted rigidity and brittleness into the fibers. Thus, if the copolymerization technique is to be successful, comonomers must be selected which either do not change

the properties of the parent fiber or which have new desirable properties of their own. This has been partially achieved in at least one case and a semi-commercial polyester is now available containing a small amount (less than 10%) of a brominated bisphenol-A to impart marginal flame resistance. It was thought that this fiber might be suitable for blending with inherently flame resistant rayon or cotton.

Flame resistant copolymers are, at least in principle, also attainable by grafting reactions. This route has had some success with cellulose but was practically untried on polyester, although there were reports of successful grafting of other types of comonomers on polyester (47).

The dispersion of a flame retardant in the spinning solution or melt prior to extrusion often circumvents some of the property losses inherent in copolymerization techniques. This method has met with some degree of success as exemplified by FMC Corporation's PFR rayon (48, 49). In this method, halogen-free alkoxy-phosphazene mixes throughout the rayon fiber in small packets or sacs; and remains stable throughout processing. With proper processing they are also not harmful to properties of the parent fiber. This approach has also been tried on an experimental basis with numerous retardants in polyester. In this case there are stringent requirements on the thermal stability of the additives since they must remain inert in the polyester melt.

Of course, for the production of flame retardant cotton the only possible approach is through chemical treatment of the yarn or loose stock. Although essentially all of the treatments developed for cotton fabrics could be adapted for such purposes, this has not yet been done on a commercial scale.

In what may ultimately prove to be a more practical approach, several investigators have shown that a reduced level of flame retardancy is obtained by blending a flammable fiber with one having inherent flame resistance. The level of flame retardancy may be greater or less than predicted from the composition of the blend. Thus the flame resistance of PFR rayon blended with cotton is reduced less than

may be expected from consideration of the blend composition (50). This effect is ascribed to the fact that the flame retardancy in the rayon is equally good for cotton and rayon and to the fact that the flame retardant effect imparted to rayon or cotton required progressively greater amounts of fire retardant to achieve higher degrees of flame resistance.

In another case, cotton fibers treated with the THPC-amide retardant to an oxygen index of 0.34 and blended 50/50 with untreated cotton with an OI of 0.18 are reported (51) to produce a blend product having an OI of 0.27, which is what one would expect from calculations. When the same fire retardant cotton fiber was blended with untreated polyester having an OI of 0.20, a 50/50 blend product exhibited an OI of 0.27. In another experiment, a predictable degree of fire retardancy was also obtained when polyester fibers were treated with tris(2,3-dibromopropyl)phosphate to an OI of 0.29 and then blended with untreated cotton having an OI of 0.18. The resulting product had an OI of about 0.24. The OI values of these particular blends are essentially the numerical averages obtained from a consideration of the oxygen index values of the respective fibers and percentage composition of the blend. These results indicated that if sufficient fire retardant of the proper type could be put in either cotton or polyester, blends of these products could exhibit good fire retardance. However, this has not been the usual observation made by various researchers. This method appears to work satisfactorily when the flame retardant fiber is present to about 65% or greater concentration. Many flame retardants for cotton are not as good for polyester/cotton blends as the THPC-amide and the tris(2,3-dibromopropyl)phosphate cited above.

2.b. Chemical Aftertreatment of Polyester/Cotton Blend Fabrics:

With the present state of technology, treatment of blend fabrics was considered as the most feasible commercially, particularly when cotton and polyester are both present to an extent of over 25%. Two approaches for the treatment of blend fabrics had been studied - use of a single fire retardant and use of two retardants in a single process.

Use of single component treatments has been most effective for the flame retardation of blends containing a large proportion of a single fiber. Thus, flame retardants designed specifically for use on polyester have their maximum effect on blends containing 80% or more polyester. Similarly, a number of the flame retardants which have been designed specifically for use on cotton can produce acceptable degrees of fire resistance in blends containing 70% or more cotton. This latter case has been studied by Hendrix and co-workers (6, 7) using oxygen index and a variety of environmental temperatures to characterize the flammability of fabrics treated with THPC-APO, a fire retardant specifically designed for use on 100% cotton. As seen in Figure 27 the OI values indicate that the retardant system is much more efficient on the 100% cotton than either of the two blends. The reason for this seemed to be connected to the fact that the flame retardant cotton component was less flammable than the ineffectively treated polyester, thus it was the polyester in this case that dictated the limits of flammability. The convergence of the OI values for the flame retardant cotton with those obtained on the blend fabrics at higher environmental temperatures simply reflected the inefficiency of the flame retardant in maintaining its effectiveness at these higher environmental temperatures. This was further illustrated in studies using the THPOH/amide finish (Figure 28) or the THPOH/ammonia finish (Figure 29) (6, 7).

One attempt to design a single compound capable of imparting flame resistance to the entire blend was reported by Tesoro and co-workers (51). They designed cellulose reactive phosphorus compounds containing sufficient bromine to reduce the flammability of both fiber components with a single flame retarding chemical. The application of N-methylol-bis(2,3-dibromopropyl)phosphonopropionamide to 50/50 polyester/cotton with an amine hydrochloride catalyst from water/dioxane solution in a conventional pad/dry/cure/wash procedure was reported (51). Although the brominated compound appeared to be insolubilized in high yield after such an application procedure and the OI was sub-

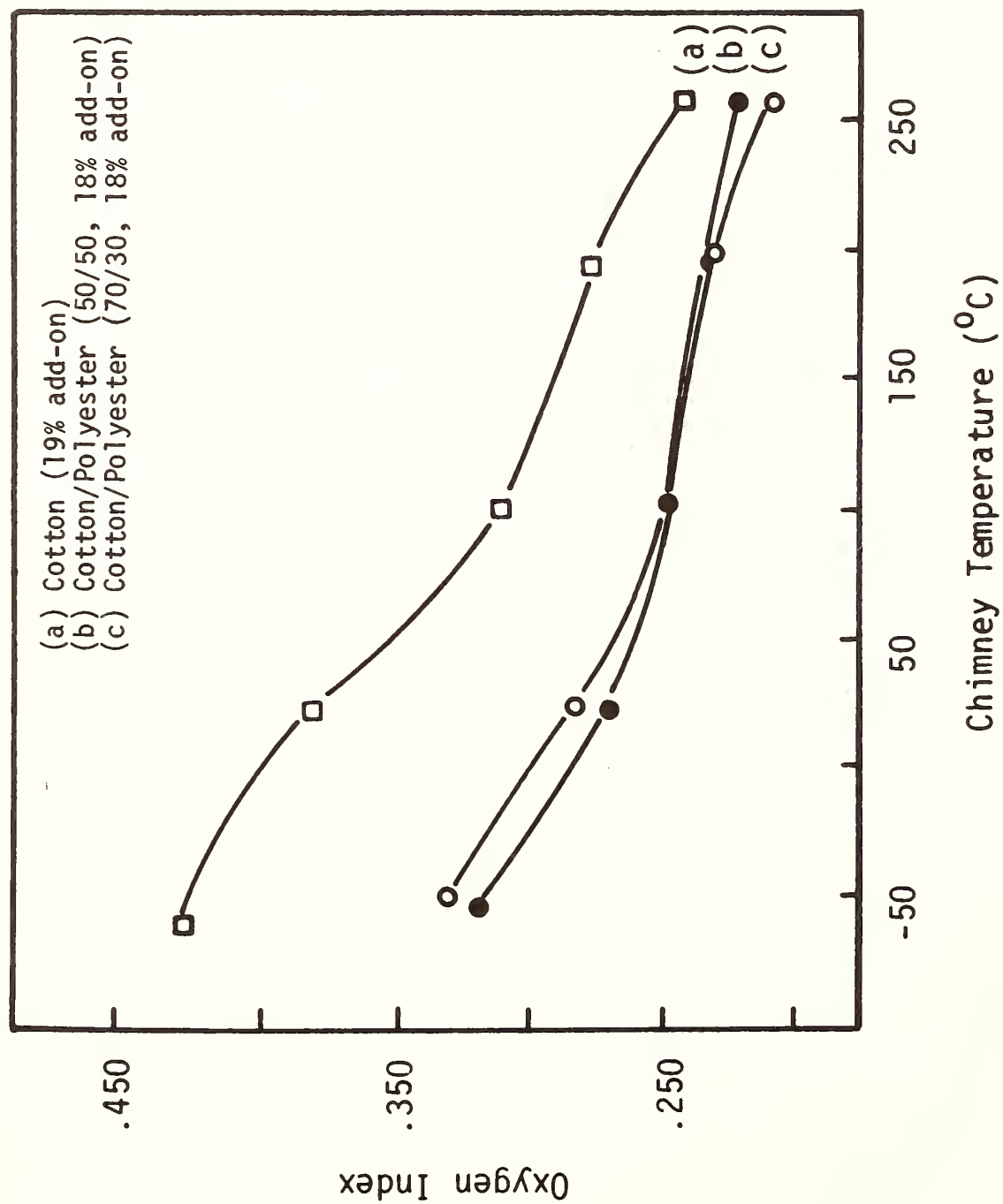


FIGURE 27. Temperature-OI relationships for fabrics (3.4 oz./yd.²) treated with THPC-AP0.

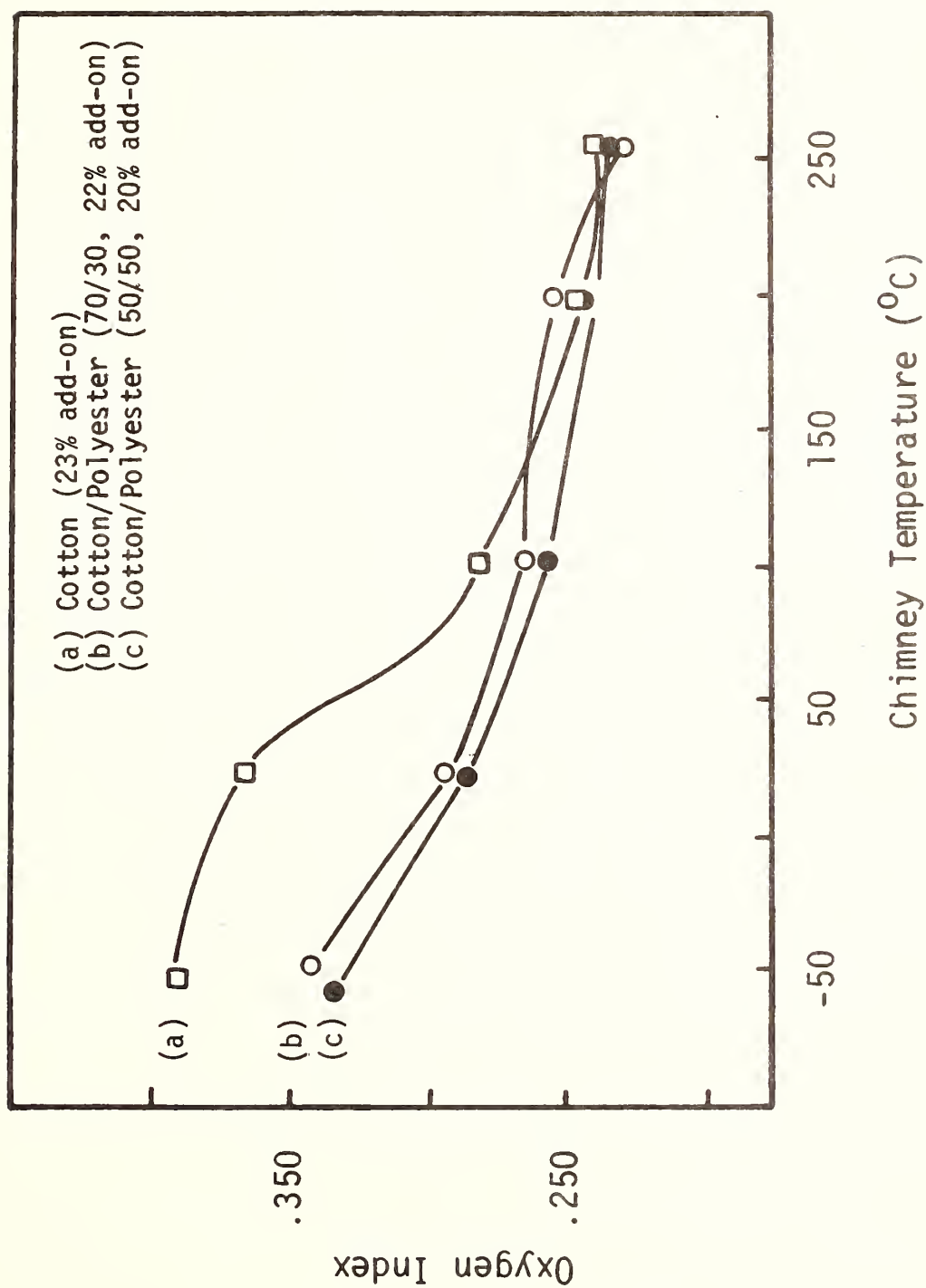


FIGURE 28. Temperature-OI relationships for fabrics (3.4 oz./yd.²), treated with THPOH/amide.

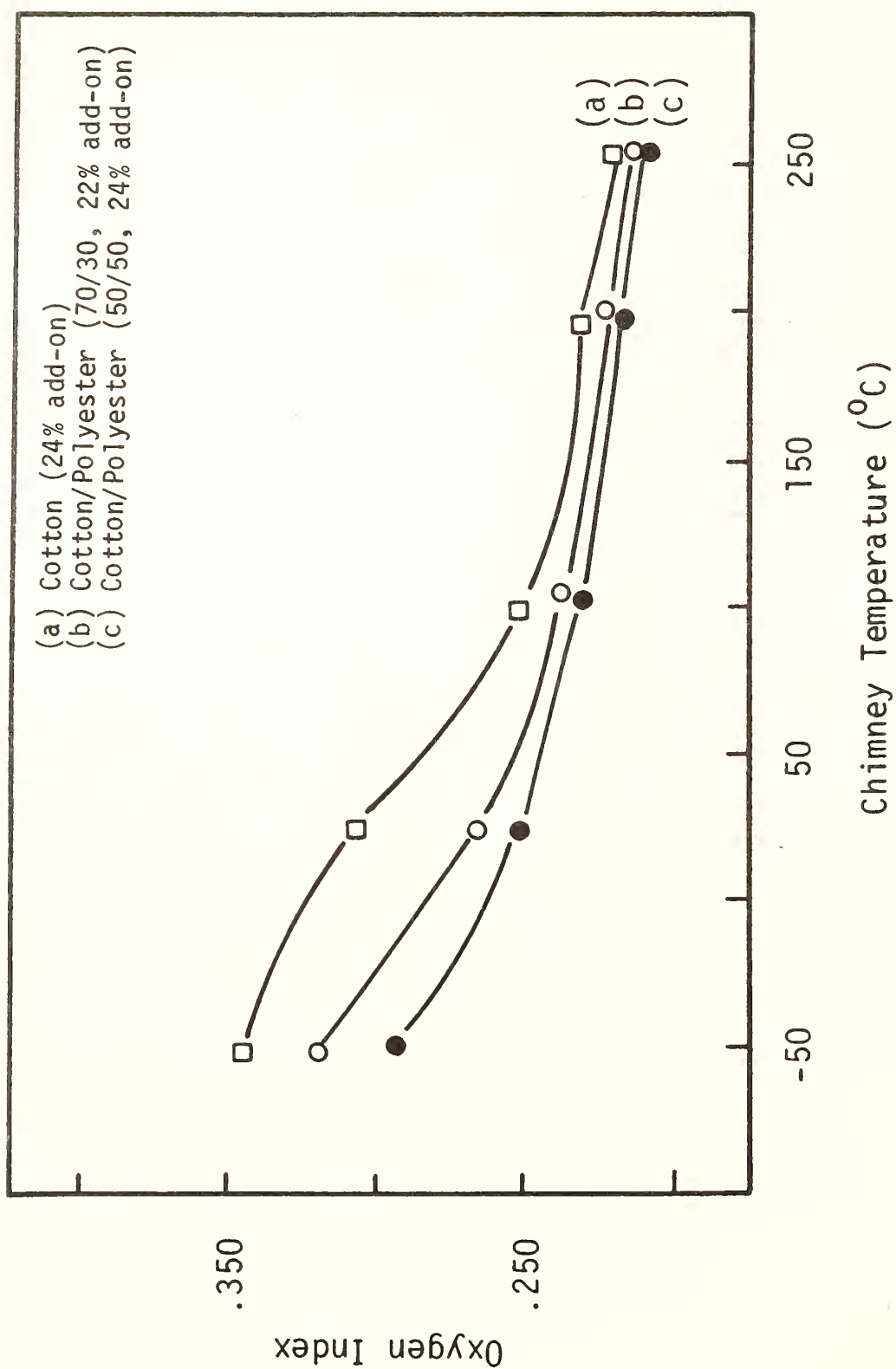


FIGURE 29. Temperature-OI relationships for fabrics (3.4 oz./yd.²), treated with THPOH/NH₃.

stantially increased, it was shown by dioxane extractions that the compound was simply deposited in the fabric rather than reacting with the cellulosic hydroxyls as would be necessary for proper durability. The authors felt that this result, along with similar results obtained with other reagents of this type, reflected inherent difficulties with respect to solubility, distribution, and/or reactivity in finishing blends with reactive organophosphorus compounds of high bromine content.

In order to circumvent this problem an alternative procedure was used in which the cotton component was reacted with an unsaturated phosphonate, and the unsaturated groups then post-brominated (51). Thus fabric samples were reacted with N-methylol-3-(diallylphosphono)propionamide in a heat-cure procedure using an acid catalyst and soaked in a solution containing a three-fold excess of bromine in chloroform. Low efficiency of the initial cellulose reaction with the unsaturated phosphonate (30-40%) was the limiting factor in this procedure although relatively high bromine contents could be obtained in the post-bromination step. Samples were reported containing up to 1.1% phosphorus and approximately 5% bromine and having OI values of 0.258. Phosphorus and bromine contents decreased about 25% in 25 launderings but the OI was not seriously affected.

These results were compared with those obtained using fabrics in which the polyester portion was specifically treated with tris-2,3(dibromopropyl)phosphate and the cotton specifically treated with N-methylol-3-(dimethylphosphono)propionamide. It appeared that such specific treatment produced a somewhat more effective flame retardancy since less reagent was needed to react a given OI value. However, it was not clear whether this was a general phenomenon or one specific for these systems.

A more successful single component treatment was that of Ciba-Geigy, A.G. based on the use of an oligomeric phosphonium salt prepared by the selfcondensation of THPC in anhydrous medium at elevated temperatures (43, 52, 53). Such oligomeric phosphonium salts applied together with a melamine resin by a pad/dry/cure technique to

polyester/cotton blends containing up to 70% polyester were claimed to result in washfast flame resistant finishes. A phosphorus content of 3.5% and 1.7-1.9% nitrogen in the fabric is recommended for durable flame retardancy. The efficiency of the phosphorus fixation was approximately 70%. Most of the finish was believed to be absorbed within the cotton fiber, but electron microscopy demonstrated that a portion of the finish was deposited on the surface of the polyester; but this portion showed good adhesion even after multiple launderings. Because of this surface deposition, the hand of the treated blends was firm; and some type of mechanical breaking was therefore recommended.

Although these single compound systems were attractive for several reasons, there were some inherent problems associated with such treatments if only one fiber was affected. When all or nearly all of the retardant must be put in one fiber in order to provide retardancy for the total composition, it frequently happens that the fiber which is treated becomes overloaded and the physical properties are changed substantially. The fabric then becomes stiff or other aesthetic properties are changed adversely.

Treatment of polyester/cotton blend fabrics with a single formulation containing two flame retardants appeared more practical. In this approach one flame retardant could be used which was especially durable and effective on cotton and a second could be used which was durable and effective on polyester. For such a system to be suitable, the retardants must be compatible in a single formulation and their cure or fixation processes must also be similar. The three processes described below represent significant progress in this area.

Bromoform Adduct of Hexaallylphosphazine with THPC-amide

This retardant was a one-bath formulation which could be applied to polyester/cotton blend fabrics with some success. The formulation was an emulsion which was applied by a pad/dry/cure process (54). The THPC-amide retardant penetrated the cotton fiber and during the heat cure formed an insoluble polymer and reacted to a modest degree with the

cellulose of the cotton. The bromoform adduct was applied to the blend fabric as a low molecular weight polymer but further polymerization occurred during the heat cure. Also, the polymer coated both the cotton and the polyester fibers.

The bromoform adduct of the hexaallylphosphazine was prepared by introducing bromoform with hexaallylphosphazine during polymerization of hexaallylphosphazine using a peroxide catalyst and polyvinyl alcohol to emulsify the system. During the reaction, bromoform added to some of the allyl groups of the hexaallylphosphazine. Other allyl groups participated in vinyl polymerization and some allyl groups remained unreacted and were available for further reaction on the fabric during the heat cure process. The emulsion contained about 30% by weight of the brominated phosphazine. This product was in an aqueous emulsion which could be added directly to aqueous THPC-amide flame retardant solutions, with which it was compatible. This combined flame retardant exhibited fairly good properties and seemed to merit further development. Its primary deficiency was the durability of the adduct. Thus, rather high add-ons were needed on 50/50 blend products to withstand 50 laundry cycles and pass the FF-3-71 test.

The amount of bromoform adduct needed was proportional to the amount of polyester in the blend fabric. The higher concentrations of the bromoform adduct were required for 50/50 polyester/cotton blends. Somewhat less of the adduct was suitable for fabrics containing 35% or less polyester.

It was found that fabrics weighing about seven ounces per square yard and containing not more than 50% polyester should contain about 20% add-on of the combined retardant in order for the fabric to pass a vertical flame test. Treated fabrics sometimes exhibited slight stiffness. The stiffening was caused mostly by the bromoform adduct; ideally prepared emulsions could cause considerable stiffness. The THPC-amide portion of this retardant which penetrates the cotton fiber was exceedingly durable to both home and commercial-type laundering as well as to drycleaning. The adduct polymer had moderate durability. It coated both cotton and polyester fibers. Some of the adduct was lost

gradually during each successive laundering, but a substantial part remained through 50 laundry cycles.

THPC-amide with tris(2,3-dibromopropyl)phosphate

This retardant was another one-bath process applicable to blend fabrics containing up to about 50% polyester (55). The emulsified combined retardant was applied to fabric by a pad/dry/cure procedure. The fabrics were padded to about a 70-80% wet pick-up then dried at about 95°C and finally cured three minutes at 160°C. Fabrics impregnated with this retardant, cured and washed frequently yellowed when treated with sodium hypochlorite bleach solution. This was due to the presence of melamine. Heavy fabrics had good aesthetic properties. However, three and one-half ounce and lighter materials generally exhibited some stiffness. Both the stiffness and discoloration would be essentially eliminated by omitting the trimethylolmelamine and using instead dimethyloldihydroxyethyleneurea, dimethylolpropyleneurea, or dimethyloluron. It took twice as much of these materials as of the trimethylolmelamine. This was due to the greater polymerization efficiency of the trimethylolmelamine and to the fact that melamine imparts a greater degree of fire retardancy per unit weight. These formulations were suitable for treatment of polyester/cotton blends in which polyester content does not appreciably exceed 50% of the fabric weight.

The THPC part of the retardant penetrated the cotton and formed an insoluble polymer and was exceedingly durable. A small amount was deposited on the surface of the polyester fiber and was lost during laundering. The tris(2,3-dibromopropyl)phosphate penetrated both the cotton and the polyester fiber and was equally good as a fire retardant on both fibers. However, the DBPP was readily removed from the cotton fiber during laundering but was durable in the polyester. Loss of the phosphate from the cotton during laundering meant that only about one half of the bromopropylphosphate remained in the textile structure to contribute fire retardancy after about fifteen laundry cycles.

The bromopropylphosphate was found to be just as effective on 100% cotton as it was on 100% polyester fabric (56). In both cases it raised the oxygen index about 0.05 units. This effect was accomplished with about 11.5% add-on and without the THPC-amide retardant. With 15% THPC-amide and without the bromopropylphosphate, the oxygen index of cotton is about 0.27 and gradually drops as the percentage of polyester is increased. Addition of 11.5% of the bromopropylphosphate to 13% THPC-amide raised the oxygen index of 100% cotton to about 0.35. Again the oxygen index gradually decreased as the polyester content was increased. This parallels the activity of the THPC-amide finish alone.

THPC-urea plus polyvinylbromide

A fire retardant based upon a blend of THPC-urea with polyvinylbromide was found effective for fabrics containing various amounts of cotton and polyester fiber (57). This retardant was applied to fabrics by a pad/dry/cure process. The THPC-urea component of this formulation was developed primarily for cotton fabrics of various weights. It represented one of the least expensive fire retardants for cotton based on THPC. The polyvinylbromide component was developed specifically for use with phosphorus-based fire retardants to extend their use to polyester/cotton blend fabrics. The polyvinylbromide was produced in emulsion so that it was compatible with aqueous fire retardant formulations.

The mole ratio of THPC to crystalline urea in the THPC-urea fire retardant had a significant influence upon durability to laundering. Since the polymerization functionality of THPC is three and that of urea is four, one would expect the greatest insolubility of the polymer and greatest durability of retardant would occur when the mole ratio of THPC to urea is about 1.3:1. This was determined to be approximately correct. During the course of the reaction of THPC with urea, one mole of formaldehyde was released which could combine with the urea. Thus a preferred mole ratio of about 1:1 was expected. This would be in the middle of the experimentally observed durable ratios. Some of PCH_2OH groups from THPC and NCH_2OH from methylolurea (formed in situ)

react with cellulose. These reactions were deemed important in aiding durability to laundering, and crosslinking cellulose through polymer structure and thus imparting wrinkle resistance to treated cellulosic fabrics. With a ratio of 1:2 the add-on was very good but the retardant was not very durable to laundering. At a mole ratio of 1:1 the add-on was just as good as with the 1:2 ratio and durability was excellent. The durability seemed to drop some when a ratio of 2:1 was used but this was partly due to the lower add-on obtained with this excess of THPC.

Disodium hydrogen phosphate was employed in this treating system for several purposes. The main value appeared to be maintenance of proper pH for reaction of PCH_2OH groups with NH groups of urea. The buffering also helped to prevent acid degradation of the cellulose. Some of the phosphate esterified the cellulose.

The polyvinylbromide concentration was also an important factor. Four percent polyvinylbromide appeared to be inadequate when used with 26% THPC-urea, assuming that the fabric must withstand 50 laundry cycles. However, 6.4% of the polymer appeared to be adequate since it gave a char length of 4.5 inches after 50 laundry cycles. With 30% THPC-urea in the formulation the amount of polyvinylbromide could be reduced to as little as 3%. All of the formulations produced fabrics with essentially no loss in breaking strength but tearing strengths were reduced about 50%.

Other factors such as drying time and temperature, curing time and temperature and use of softening agents were also important. These have been recently reviewed by Reeves and co-workers (50).

All of this leads to the conclusions that a great deal was known about flame retardance of cotton and polyester and that some beginnings had been made to develop treatments for blends by June 1974. However, a great deal remained to be done before commercially feasible systems could be formulated.

TESTING METHODOLOGY

In attempting to evaluate existing flame retardant treatments for 50/50 polyester-cotton blend fabrics a primary concern is that of appropriate testing methodology. This is also a basic factor in trying to set goals for the research work. The flammability or flame resistance of the samples must be judged in a manner that produces information relative to the ultimate utilization and marketability of the treated fabrics. Since it had been decided that the fabrics to be studied would be those which are encountered in general apparel uses, this would require that the test methods be as closely related as possible to those which will be used to evaluate general apparel in the marketplace. However, it must be recognized that these markets are completely reliant on government regulations and without such regulations there would probably be only a very small market for flame retardant apparel. Thus the tests which are appropriate are those prescribed by the U. S. Consumer Product Safety Commission; but at present CPSC has not indicated exactly which test or method it will prescribe. For this reason, it was decided that dual goals should be established for the ETIP research project and all candidate systems were, therefore, evaluated in terms of their ability to produce fabrics which would pass the requirements of the childrens' sleepwear standard for sizes 7-14 (FF 5-74) and which could meet the criteria for classification as class I on the Mushroom Apparel Flammability Tester (MAFT) as described in the recommendations made by NBS to CPSC in March, 1976.

1. Oxygen Index and 45° Angle Burning Tests

Unfortunately, neither of the standard test methods is capable of detecting subtle changes in flame retardant effectiveness and thus neither is adequate for the needs of flame retardant research. Thus other more sensitive tests must be used in the research work but these tests must be relatable to the MAFT and FF 5-74. The most obvious candidate for this would seem to be the oxygen index (OI) method. It has been utilized extensively in the early phases of the ETIP project but it was soon found that, in its standard top ignition mode; it was not always an accurate reflection of the behavior which the samples would exhibit in vertical upward burning in either the MAFT or FF-5. Other workers have apparently reached similar conclusions recently.

A subjective burning test was thus developed using a 2" x 5" sample mounted on a pin frame supported at an angle of 45° from the vertical and ignited on the bottom edge using a wooden kitchen match. This seemed to give important information on the overall flammability of the samples and proved to be a valuable adjunct to the OI. In several cases pairs of samples were found which gave similar results on FF-5 or OI but which exhibited grossly different burning characteristics on the 45° frame; both would burn the entire length but one sample would burn rapidly over the width of the sample with a large frame whereas the other would burn slowly over a narrow strip with a small frame. These fabrics would obviously pose significantly different levels of hazard to the consumer.

Presumably the difference in behavior between the OI and the 45° of FF-5 tests is due to a difference in geometry of burning. Thus an attempt was made to develop a reproducible technique for measuring the oxygen index using bottom ignition (BOI) in a manner similar to that previously reported in the literature (58). That this can be done in a reproducible manner is indicated by the data in Table III. These data also indicate that some flame retardants are more sensitive than others to changes in geometry. This is re-

TABLE III
COMPARISON OF TOP AND BOTTOM OXYGEN INDEX METHODS

	% P	OI	BOI	BOI ²
65/35 DAP	4.0	28.8	20.5	20.5
	2.8	27.0	20.0	----
	2.1	----	19.2	19.5
	1.7	----	18.5	----
	1.3	23.5	18.5	18.2
50/50 DAP	4.5	31.5	21.8	21.5
	3.3	28.8	20.0	----
	2.4	----	20.0	19.8
	2.1	----	20.0	19.5
	1.4	23.5	19.5	19.0
65/35 Antiblaze [®] 19	3.0	25.0	19.5	----
	2.2	23.0	18.2	18.2
	1.5	22.2	----	17.8
	0.89	21.2	----	16.8
50/50 Antiblaze [®] 19	3.2	25.5	23.0	----
	2.2	23.8	20.0	19.8
	1.6	----	19.0	18.8
	1.2	22.5	18.5	18.2
	0.9	----	18.0	17.5

BOI² - second determination at least 24 hours later.

lated to the mechanisms of action of the retardants and is discussed in detail in later sections.

A number of reference compounds have now been studied in this fashion and the results of these studies are given in Table IV. Also included in this table are observations based on 45° burning tests and isoperibol calorimetry. On the basis of this limited data set, it appears that oxygen index using BOI is a more accurate indicator of the way a sample will perform in normal atmosphere burning tests. The limit for burning in the 45° angle test as it is performed at Clemson has been found to be between 19.5 and 20.5 for BOI as compared to 25.0 and 28.0 for normal oxygen index using top ignition. Because of the flow environment, isoperibol calorimetry appears to be an even more stringent test than the 45° angle burning. The limit for burning in the isoperibol is apparently indicated by a BOI between 21.0 and 22.0 with the samples studied to date.

These data indicate that there are two different types of flame retardant response as indicated by OI and BOI. In the first category, represented by retardants such as dibromopropyl phosphate and DAP, the OI increases much faster than the BOI as the add-on level increases. In the second category represented by compounds such as N-methylol-3-(diphenylphosphinyl) propinamide (MD3P) fixed with a melamine resin, Pyrovatex[®] 3762 and Antiblaze[®] 19, the OI and BOI increase at approximately the same rate. It is interesting to note that these latter compounds have been found to have a much smaller effect on the heat release values as measured by an isoperibol calorimeter than those which fall into the former category.

2. Calorimetric Measurements

Both static oxygen bomb (SOB) and isoperibol calorimetry have been found in previous work to constitute powerful probes into both mechanisms and efficiency characteristics of flame retardant action (59). In an attempt to utilize these techniques more fully in the present work, efforts were made to develop a more complete interpre-

TABLE IV

COMPARISON OF FLAMMABILITY TEST METHODS

	% P	Fabric	OI	BOI	45°	Isoperibol
Control	0	50/50	17.8	15	burned	burned
	0	65/35	18.0	15.5	burned	burned
Diammonium phosphate	4.5	50/50	31.5	21.8	DNB ⁽¹⁾	DNB
	3.3	50/50	28.8	20.0	DNB	DNB
	2.4	50/50	26.2	19.8	IR ⁽²⁾	IR
	4.0	65/35	28.7	20.5	DNB	DNB
	2.8	65/35	27.0	20.0	DNB	DNB
Tris 2,3(Dibromopropyl)- phosphate	2.1	65/35	24.8	19.3	IR	burned
	1.69	50/50	29.2	21.0	DNB	DNB
	1.13	50/50	26.5	19.5	DNB	IR
	0.83	50/50	25.0	19.0	IR	burned
	0.56	50/50	23.0	18.0	burned	burned
	1.75	65/35	30.0	20.5	DNB	DNB
	1.18	65/35	27.0	18.5	DNB	IR
	0.84	65/35	26.5	18.0	IR	burned
	0.58	65/35	24.5	17.5	burned	burned

TABLE IV (Cont.)

	% P	Fabric	OI	BOI	45°	Isoperibol
MD3P (fixed)	2.72	50/50	24.8	20.5	DNB	DNB
	1.21	50/50	22.2	18.5	burned	burned
	2.25	65/35	24.2	19.5	IR	IR
	1.05	65/35	22.0	17.0	burned	burned
Antiblaze ^(R) 19	3.2	50/50	25.5	20.5	DNB	IR
	2.2	50/50	23.8	18.5	IR	burned
	1.6	50/50	22.5	18.0	burned	burned
	1.2	50/50	22.5	17.5	burned	burned
Pyrovatex 3762	3.9	50/50	27.1	22.0	DNB	DNB
	2.7	50/50	25.6	21.0	DNB	IR
	2.05	50/50	25.2	19.0	IR	burned
	1.24	50/50	22.5	18.0	burned	burned
	3.72	65/35	26.7	21.5	DNB	DNB
	2.31	65/35	26.0	20.0	DNB	IR
	1.87	65/35	25.3	19.0	IR	burned
	1.12	65/35	23.1	18.2	burned	burned

(1) Did not burn

(2) Ignition resistant

tation of the calorimetric data in terms of the general principles of flame retardant action. It has generally been accepted that the burning of polymeric materials is a cyclic process. A simplified diagram of this cyclic burning process is schematically shown in Figure 30. The process starts with the initial heat input (ignition source) to the polymer substrate, which raises the temperature of the substrate and triggers its thermal decomposition. Combustible gases which are generated as the result of the degradation of the substrate combine with the proper amount of oxygen from the surrounding atmosphere and, with proper ignition source, a rapid oxidation process (combustion) takes place. As the result of the combustion process, heat is given off, although a fraction of the combustible gases escape without being completely oxidized. Part of the heat generated from the combustion process is transferred to the surrounding environment, while the rest is fed back to the substrate to further promote the pyrolysis process and thus completes the cycle. There are two distinct types of processes involved, those in the substrate which can be regarded as fuel generating, and those in the gaseous phase which can be regarded as fuel consuming. Thermodynamically, there are two distinct parameters associated with these two processes (Figure 31) : 1) the heat value of the combustible gases generated (ΔH_2) which is associated with and is essentially controlled by the fuel-generating processes and, 2) the actual heat released (ΔH_1) which is mainly controlled by the combustion (heat consuming) processes. It is generally believed that there are two types of chemical flame retardants: 1) a condensed phase active retardant which is effective in the substrate and reduces the amount of combustible gases generated, presumably by retarding or altering the normal degradation process and, 2) vapor phase retardant which is active in the gaseous combustion process and reduces the actual amount of heat generated, presumably by retarding the oxidation reactions through free-radical termination and radical recombination processes. The effect of each of these two types of retardant on the entire burning process and particularly on the two parameters mentioned above, can be

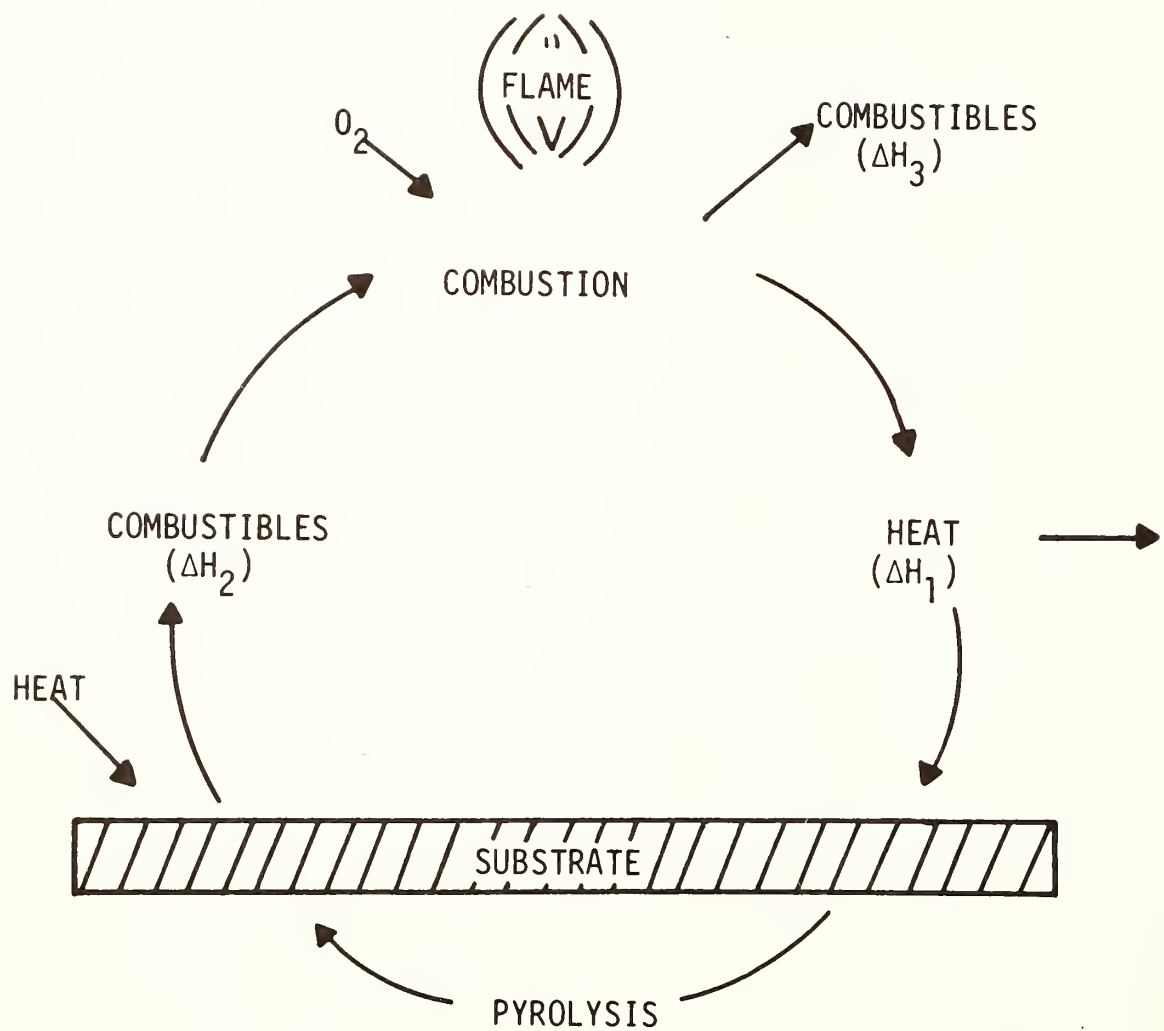
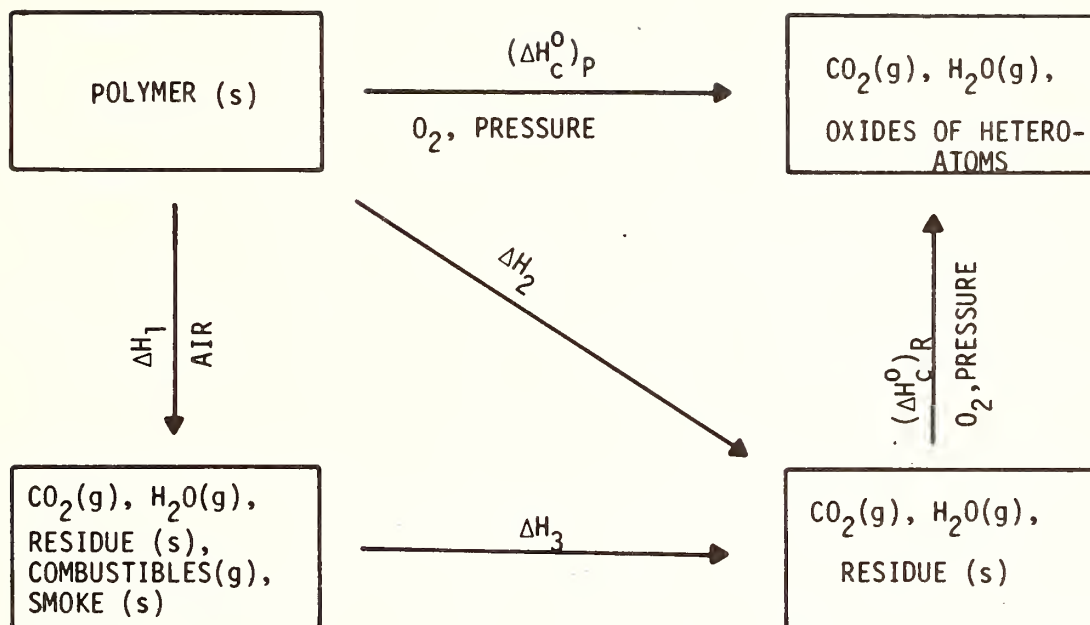


FIGURE 30. Diagram of polymer fire.



$$(\Delta H_C^0)_P = \Delta H_2 + R (\Delta H_C^0)_R$$

$$\Delta H_2 = \Delta H_1 + \Delta H_3$$

where

$(\Delta H_C^0)_P$ = Heat of Combustion of Polymer, cal/gm Polymer

$(\Delta H_C^0)_R$ = Heat of Combustion of Residue, cal/gm Residue

ΔH_1 = Actual Heat Released in Air, cal/gm Polymer

ΔH_2 = Total Net Fuel Generated, cal/gm Polymer

ΔH_3 = Heat of Combustion of Combustibles, cal/gm Polymer

R = Weight Fraction of Residue from Burning in Air

FIGURE 31. Calorimetric combustion scheme.

rationalized as follows:

1) A retardant system active only on the fuel generating processes: the retardant action is strictly on the degradation processes; the heat values of combustible gases generated (ΔH_2), or the fraction of fuel value $\{\Delta H_2/(\Delta H_C^0)_F\}$ decreases as a function of increasing retardant content, and as a result, actual heat generated (ΔH_1) or $\{\Delta H_1/(\Delta H_C^0)_F\}$, also decreases as a function of increasing retardant content.

However, since the combustion processes are not affected by the presence of retardant, the ratio $\Delta H_1/\Delta H_2$ should remain constant and is independent of retardant content.

2) A retardant system active only on the fuel consuming processes: The retardant action is limited to the combustion processes, thus the ratio, $\Delta H_1/\Delta H_2$ should decrease as a function of retardant content, and since the pyrolysis is not affected by the presence of the retardant, $\Delta H_2/(\Delta H_C^0)_F$ should remain constant and is independent of retardant content.

3) A retardant system with combined action in both fuel generating and consuming processes: both the degradation and combustion processes are affected by the retardant, thus both the ratio $\Delta H_1/\Delta H_2/(\Delta H_C^0)_F$ should decrease as a function of retardant content.

It is clear from the above rationalizations that these two parameters, ΔH_1 and ΔH_2 , could be used to elucidate the mode of the retardant action. And both ΔH_1 and ΔH_2 can be obtained calorimetrically as shown in Figure 31 while ΔH_1 is directly measured with the isoperibol calorimeter, and ΔH_2 , indirectly by the oxygen bomb calorimeter.

A series of flame retardant treated fabrics, 100% cotton, 50/50 and 65/35 polyester/cotton blends, have been studied with both calorimetric techniques. The flame retardants include a variety of experimental and commercial retardants containing phosphorus and/or halogen. Heat release data (ΔH_1) measured with the isoperibol and the fuel

value (ΔH_2) obtained as the difference of the heats of combustion of the fabric and the char were used to test the validity of the above suppositions. Both ΔH_1 and ΔH_2 , as well as the combustion efficiency ($\Delta H_1/\Delta H_2$), from these systems were tabulated in Table V. The fuel generation (ΔH_2) and the heat release (ΔH_1) values were presented as a fraction with respect to the total fuel value of the system, $\Delta H_2/(\Delta H_C^0)_F$ and $\Delta H_1/(\Delta H_C^0)_F$ respectively. $(\Delta H_C^0)_F$ is the heat of combustion of the treated fabric and is used to normalize both ΔH_1 and ΔH_2 , since the total fuel value of the system changes with the addition of flame retardant.

The results shown in Table V indicates that, based on the rationalization presented above, all the phosphorus-containing retardants investigated $\{H_3PO_4, (NH_4)_2HPO_4, THPOH-NH_3$ and $THPC/urea\}$ are condensed phase active, whereas the halogen-containing retardants (T23P, P-44, PVBr and $P(VBr/VCl)$) are vapor phase active. The combustion efficiency, $\Delta H_1/\Delta H_2$, from each of the condensed phase active systems is constant, independent of the phosphorus content in the system. While values of $\Delta H_1/(\Delta H_C^0)_F$ and $\Delta H_2/(\Delta H_C^0)_F$ decrease with the phosphorus content. However, the decrease is much less profound in the blends than in 100% cotton, indicating that the retardant is only effective on the cellulosic component of the system. Each of the vapor-phase active system generates a constant fraction of the fuel, $\Delta H_2/(\Delta H_C^0)_F$, regardless of the halogen content, whereas both the combustion efficiency, $\Delta H_1/\Delta H_2$, and the fraction of the heat released, $\Delta H_1/(\Delta H_C^0)_F$, decrease with increasing halogen content. For poly (vinyl bromide) (PVBr) and a copolymer of vinylbromide and vinylchloride $\{P(VBr/VCl)\}$ the decrease in $\Delta H_1/\Delta H_2$ and $(\Delta H_C^0)_F$ is almost insignificant, though the trend of decreasing is there. This is the indication of the inefficiency of these two retardants. This is discussed in detail in the section beginning on page 356.

In addition to these attempts to establish a fundamental basis for the mechanistic interpretation of the isoperibol calorimetric results, efforts have also been expended to assure the accuracy of the heat release values. This was considerably complicated by the

TABLE V
CALORIMETRIC PARAMETERS OF VARIOUS TREATED SYSTEMS

% P	% Br	$\Delta H_1 / (\Delta H_C^O)_F$	$\Delta H_2 / (\Delta H_C^O)_F$	$\Delta H_1 / \Delta H_2$
H_3PO_4 on 100% cotton				
0.56	----	0.52	0.56	0.92
0.77	----	0.47	0.51	0.92
1.03	----	0.42	0.45	0.92
1.38	----	0.37	0.40	<u>0.92</u>
				Ave. 0.92
$(NH_4)_2HPO_4$ on 100% cotton				
0.49	----	0.52	0.59	0.88
0.81	----	0.42	0.48	0.88
0.93	----	0.40	0.45	0.89
1.11	----	0.36	0.41	<u>0.89</u>
				Ave. 0.89
THPOH-NH ₃ on 100% cotton				
0.15	----	0.71	0.79	0.89
0.53	----	0.52	0.58	0.89
0.98	----	0.42	0.48	0.89
2.23	----	0.30	0.33	<u>0.89</u>
				Ave. 0.89
P-44 on 100% cotton				
----	2.01	0.73	0.97	0.75
----	3.04	0.69	0.96	0.69
----	3.68	0.64	0.94	0.68
----	4.26	0.67	0.96	0.67
----	6.23	0.54	<u>0.94</u>	0.58
				Ave. 0.95
$(NH_4)_2HPO_4$ on 50/50 Blend				
0.72	----	0.49	0.78	0.63
1.12	----	0.47	0.78	0.63
1.51	----	0.47	0.74	0.64
2.31	----	0.47	0.72	0.65
2.60	----	0.46	0.69	0.64
3.14	----	0.43	0.68	<u>0.64</u>
				Ave. 0.64

TABLE V (con't)

% P	% Br	$\Delta H_1/(\Delta H_C^0)_F$	$\Delta H_2/(\Delta H_C^0)_F$	$\Delta H_1/\Delta H_2$
THPC/urea on 50/50 Blend				
1.20	----	0.42	0.72	0.57
1.80	----	0.37	0.67	0.55
1.90	----	0.38	0.68	0.57
2.41	----	0.37	0.64	0.57
2.50	----	0.36	0.65	0.56
3.51	----	0.34	0.62	0.55
				Ave. 0.56

(NH₄)₂HPO₄/T23P on 50/50 Blend (1% P as DAP)

1.0	2.48	0.43	0.75	0.58
1.0	4.48	0.39	0.73	0.53
1.0	7.50	0.34	0.73	0.47
1.0	9.70	0.30	0.73	0.45

THPC/urea/PVBr on 50/50 Blend (1% P as THPC)

1.0	3.12	0.39	0.74	0.53
1.0	4.19	0.39	0.74	0.53
1.0	6.15	0.38	0.73	0.50
1.0	9.58	0.33	0.72	0.45
				Ave. 0.73

THPC/urea/VBr-VC1 on 50/50 Blend (1% P as THPC)

1.0	1.28	0.41	0.74	0.56
1.0	2.51	0.41	0.75	0.54
1.0	3.43	0.39	0.74	0.53
1.0	4.71	0.37	0.74	0.51
				Ave. 0.74

P-44 on 50/50 Blend

----	1.89	0.51	0.89	0.58
----	4.30	0.48	0.93	0.52
----	4.48	0.48	0.92	0.52
				Ave. 0.91

P-44 on 65/35 Blend

----	1.67	0.47	0.86	0.55
----	2.70	0.46	0.86	0.53
----	3.73	0.42	0.87	0.49
----	5.22	0.39	0.85	0.46
----	5.68	0.36	0.83	0.43
				Ave. 0.85

finding that the ΔH_1 values are subject to some unusual effects when the fabrics are supported by a fiber glass veil. The presence of this veil seems to increase the heat release from the blends but the nature of this effect is not well understood at present. In order to determine whether this effect is an experimental artifact or a significant fabric property, a series of fabrics was evaluated with and without the glass veil. Samples of these same fabrics were also sent to the National Bureau of Standards for evaluation on the MAFT.

A series of untreated blends containing various ratios of cotton and polyester were reevaluated with the fiber glass support and the results are shown in Table VI and Figure 32. The results obtained with the glass support showed a considerable decrease in residue with a concurrent increase in both amount of heat released and rate of heat evolution. The increase in heat evolution ranged from essentially zero for the 100% cotton fabric to approximately 1100 calories for the 100% polyester. In all cases the presence of the glass support increased the rate of heat release by approximately 20 calories/sec-cm. It would appear that this effect might be attributable to several factors; the most obvious is the fact that the glass support significantly restricts the flow of molten polyester thus increasing its rate of pyrolysis and completeness of combustion. A second factor could be the possibilities which exist for increased heat conduction through the glass veil thus causing an increase in preheating of the polymer ahead of the flame front. Thirdly, the effect could be due to the action of the grid underlay as a thermal shield which would delay initial heat transfer from the burning sample to the calorimeter giving an anomalously high heat release rate. If this were the case the symmetry of the heat transfer from the sample would also be disturbed resulting in a distortion of the normal heat transfer pattern which is experienced by the calorimeter during calibration. On the basis of initial results, however, it would seem that these latter two factors are of only minimal importance because of the small variations observed in both rate and heat release from the 100% cotton fabrics where melt and drip would not be involved.

TABLE VI

ISOPERIBOL RESULTS OF PET/COTTON BLENDS

% COTTON	% RESIDUE ⁽¹⁾	RATE, cal/sec-cm ⁽¹⁾	-ΔH _f , cal/gm ⁽¹⁾
100.0	--	79.9 (82.9)	3334 (3423)
87.5	--	75.6 (95.1)	3047 (3312)
75.0	--	71.3 (89.2)	2926 (3328)
62.5	5.5 (2.4)	66.0 (84.2)	2755 (2943)
50.0	6.6 (4.5)	62.0 (83.4)	2767 (3007)
35.0	8.7 ⁽²⁾ (5.4)	54.2 ⁽³⁾ (76.0)	2846 ⁽²⁾ (3034)
20.0	7.6 ⁽³⁾ (5.1)	45.4 ⁽³⁾ (61.5)	3183 ⁽³⁾ (3480)
0.0	41.9 ⁽³⁾ (9.8)	--	2188 ⁽³⁾ (3274)

(1) Values in parentheses are those supported with fiberglass grid.

(2) Supported with 3 metal wire stitches.

(3) Supported with fiberglass gauze.

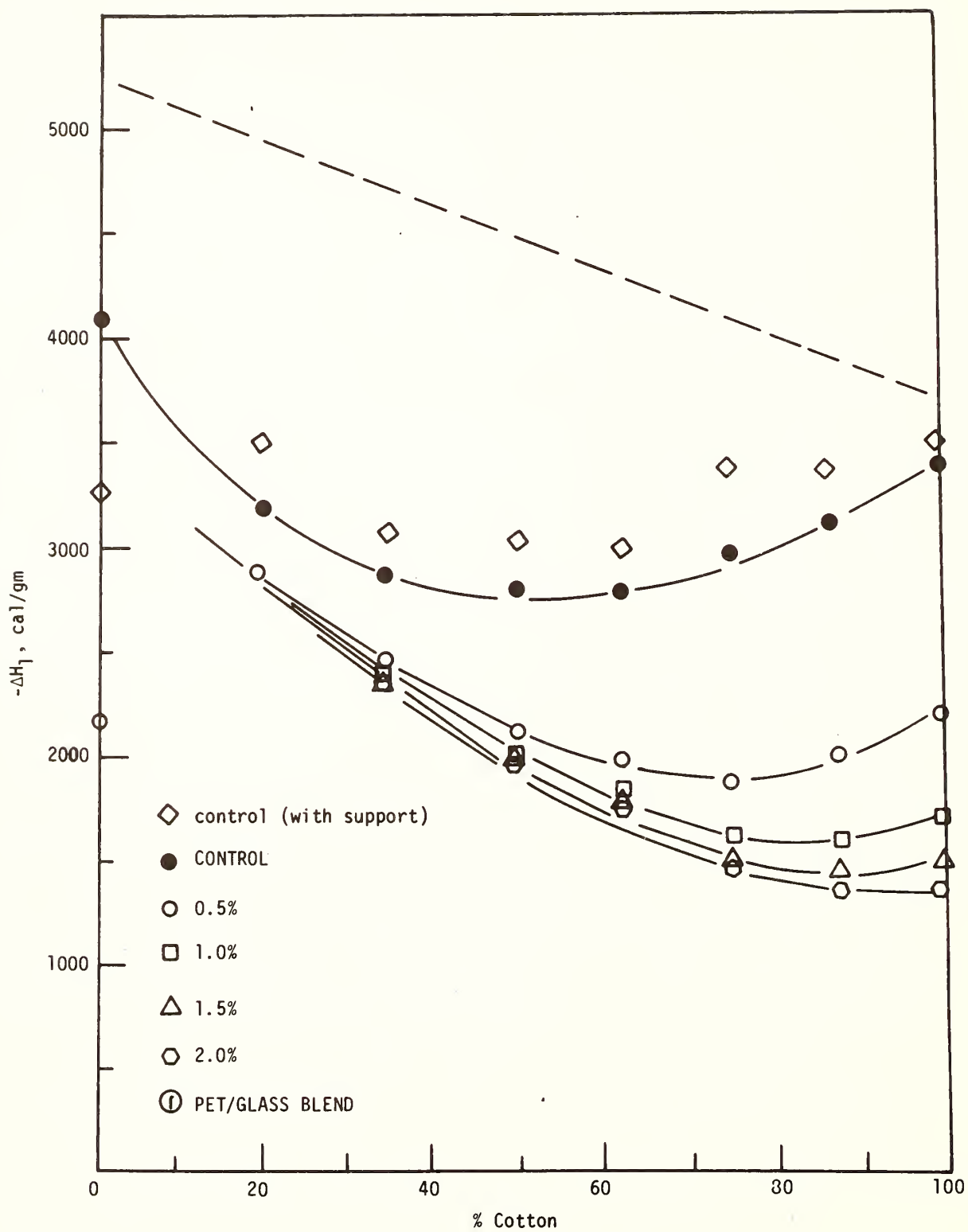


FIGURE 32. Heat release of PET/cotton blends burned with and without support.

The magnitude of the effect due to the grid appears to decrease with increasing levels of condensed phase active flame retardant on the cotton portion of the blend. This can be seen from the results of a series of investigations on fabrics treated with increasing levels of diammonium phosphate with and without the fiber glass support. These results are tabulated in Table VII, and the heat release results are shown in Figure 33. The presence of the glass support can be seen to increase the heat release by approximately 500 calories. However, this difference decreases with increasing levels of phosphorus in the cotton and there is essentially no difference for samples with more than 2% phosphorus content. It would appear that this is because there is enough char formed from cotton containing 2% or more phosphorus to support combustion of the polyester and prevent any melt flow. The additional support provided by the fiber glass does not seem to be of any significance. The effect of the grid upon the rate of heat release appears to be more complicated. Visual observation indicates that the flame does not break through the glass grid and thus only the top half of the calorimeter directly receives heat from the burning sample. This could cause the recorded time-temperature curve to shift up the time scale, and would result in a lower rate of heat release, as observed. Such behavior is different from that observed with the untreated blend when there was initial delay followed by the intense heat release from the burning sample breaking through the glass grid.

In order to explore the nature of these effects more deeply, samples of 100% cotton and 50/50 polyester/cotton blend fabrics were treated with antimony oxide, decabromodiphenyl oxide and an acrylic binder (FR-P-44 from White Chemical Company) and evaluated in the isoperibol calorimeter. The results obtained using the fiber glass support are given in Table VIII. These heat release values were plotted versus calculated % bromine as shown in Figure 34. Previous results without the support are also included for comparison. The effect of using the support was found to be an increase in heat release in these two series. This is the opposite of that observed

TABLE VII
ISOPERIBOL RESULTS OF DIAMMONIUM PHOSPHATE TREATED 50/50 POLYESTER/COTTON

% P	% Residue	Rate, cal/sec-cm*	-ΔH ₁ , cal/gm.
Control (ETIP)	8.3 (3.4)	46.2 (63.4)	2942 (3460)
0.72	15.2 (14.1)	60.3 (56.6)	2224 (2419)
1.12	17.6 (15.0)	60.6 (52.3)	2126 (2391)
1.52	19.4 (17.3)	61.1 (49.1)	2097 (2318)
2.31	21.7 (19.5)	54.5 (46.8)	2059 (2077)
2.60	23.6 (20.5)	48.6 (45.5)	1964 (2021)
3.14	25.8 (25.0)	52.7 (35.7)	1819 (1868)

*Values in parenthesis are those supported with fiber-glass grid.

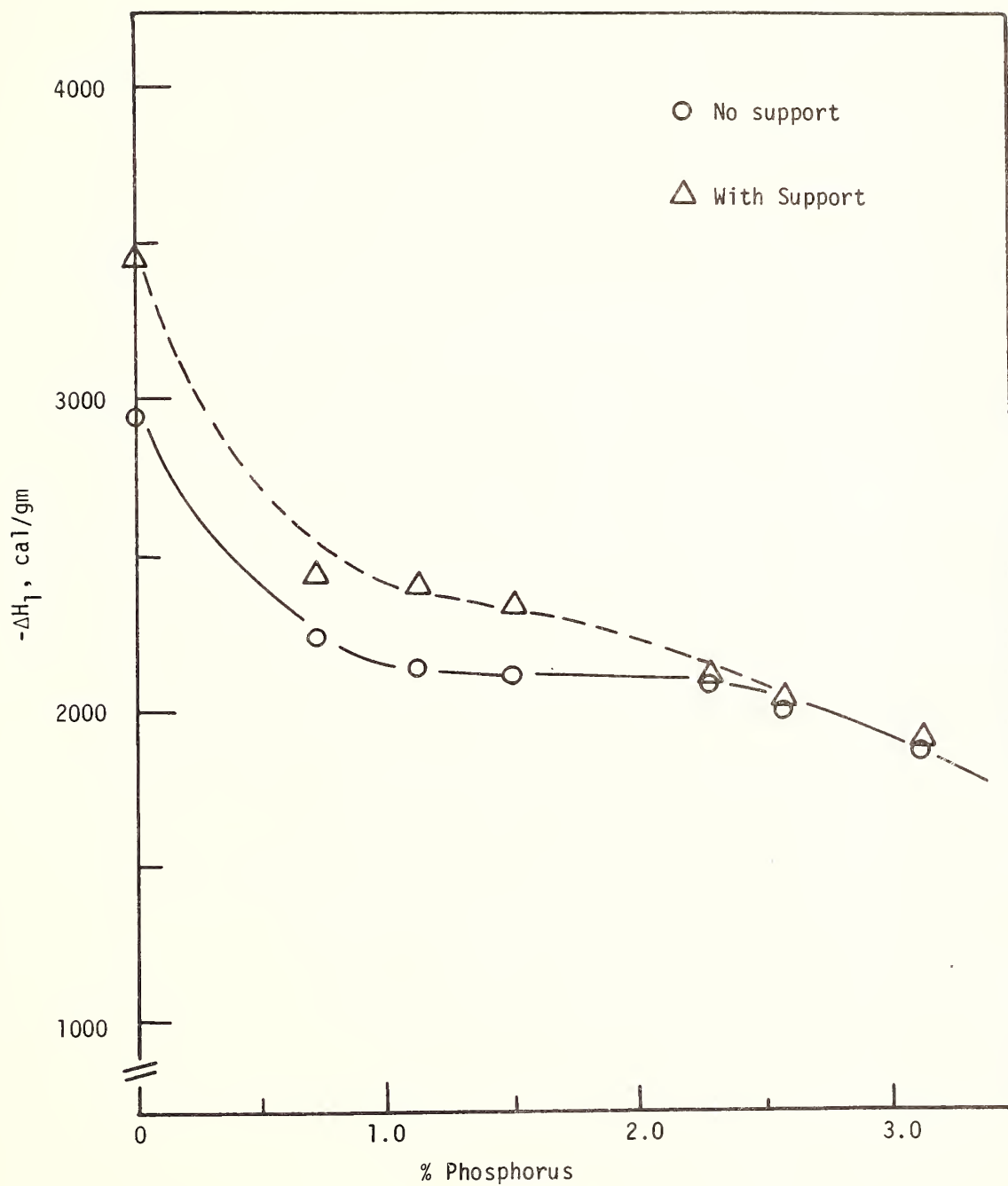


FIGURE 33. Heat-release of diammonium phosphate treated ETIP blend burned with and without fiber-blass support.

TABLE VIII
CALORIMETRIC DATA OF DECABROMODIPHENYL OXIDE TREATED FABRICS WITH FIBER-GLASS-GRID SUPPORT

% Finish	Calc % Br	Analyzed % Br	% R	Rate, cal sec/cm	$-\Delta H_f$, cal/gm	$\Delta H_f - (\Delta H_f)$ control cal/gm
<u>100% Cotton</u>						
Control	-----	-----	---	82.9	3424	0
5.80	4.83	2.64	---	77.8	3138	286
6.35	5.29	2.70	---	75.3	2983	441
9.54	7.95	4.18	1.6	71.8	2746	678
12.24	10.20	4.27	2.6	65.4	2445	979
14.57	12.14	4.94	2.1	57.4	2239	1185
<u>50/50 Polyester/Cotton</u>						
Control	-----	-----	3.4	63.4	3460	0
5.98	4.98	2.38	5.6	60.6	2814	746
9.94	8.28	3.78	7.2	48.1	2449	1011
13.20	11.00	4.97	8.3	38.6	1939	1521
16.41	13.67	6.34	8.2	27.8	1651	1809

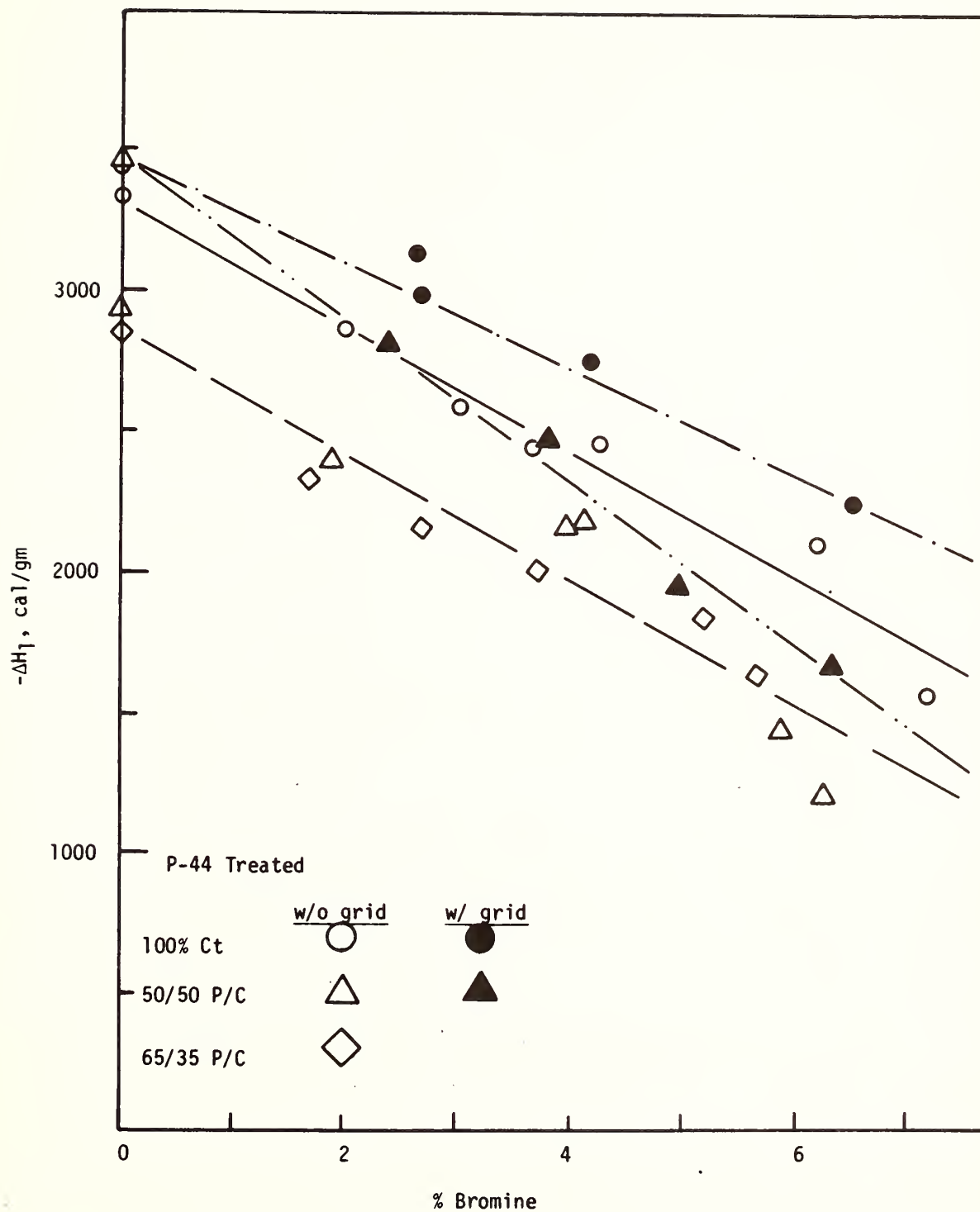


FIGURE 34. Heat release of P-44 treated fabrics.

with the diammonium phosphate treatments. The DAP treated blend fabric showed a difference between the heats observed with and without support which decreased with increasing %P content in the fabric; there was essentially no difference with treatment levels above 2%P. However, current data on P-44 treated fabrics show a difference in heat release between the supported and unsupported samples which increase with increasing %Br content in the fabric. Similar results were also observed on P-44 treated fabrics of 100% cotton where additional physical support from the grid is not expected to have significant effect on the heat release. These results tend to suggest that the presence of the grid may have caused premature loss of flame retardant by vaporization. The grid, acting as a thermal shield could channel the hot convective current upward ahead of the flame, thus increasing the pre-heating of the fabric and causing the vaporization of flame retardant ahead of the flame zone.

The net heat reductions, $\Delta H_1 - (\Delta H_1)_{\text{control}}$, of these series are shown in Figure 35. Previous data obtained without support showed that P-44 has identical efficiencies on cotton and the blend; the net heat reductions from both cotton and the blend showed identical dependence on the %Br content. However, in the current series with the support, P-44 seems to be more efficient on the 50/50 blend than on the 100% cotton. This could be due to the melting of the polyester in the blend which might cause the fabric to sag and make contact with the grid. Although the contact would provide additional physical support to the burning polyester and thus increase its combustion, it would also hinder any upward convective current between the fabric and the grid.

There is essentially no char formed by these fabrics which is consistent with the earlier indications that P-44 is a completely vapor-phase active retardant. The effect due to the physical support provided by the grid is thus expected to be independent of the retardant content in the sample for a given type of fabric. For the blend, the difference in heats observed with and without the grid is constant up to about 6%Br. This is evidently due to the physical

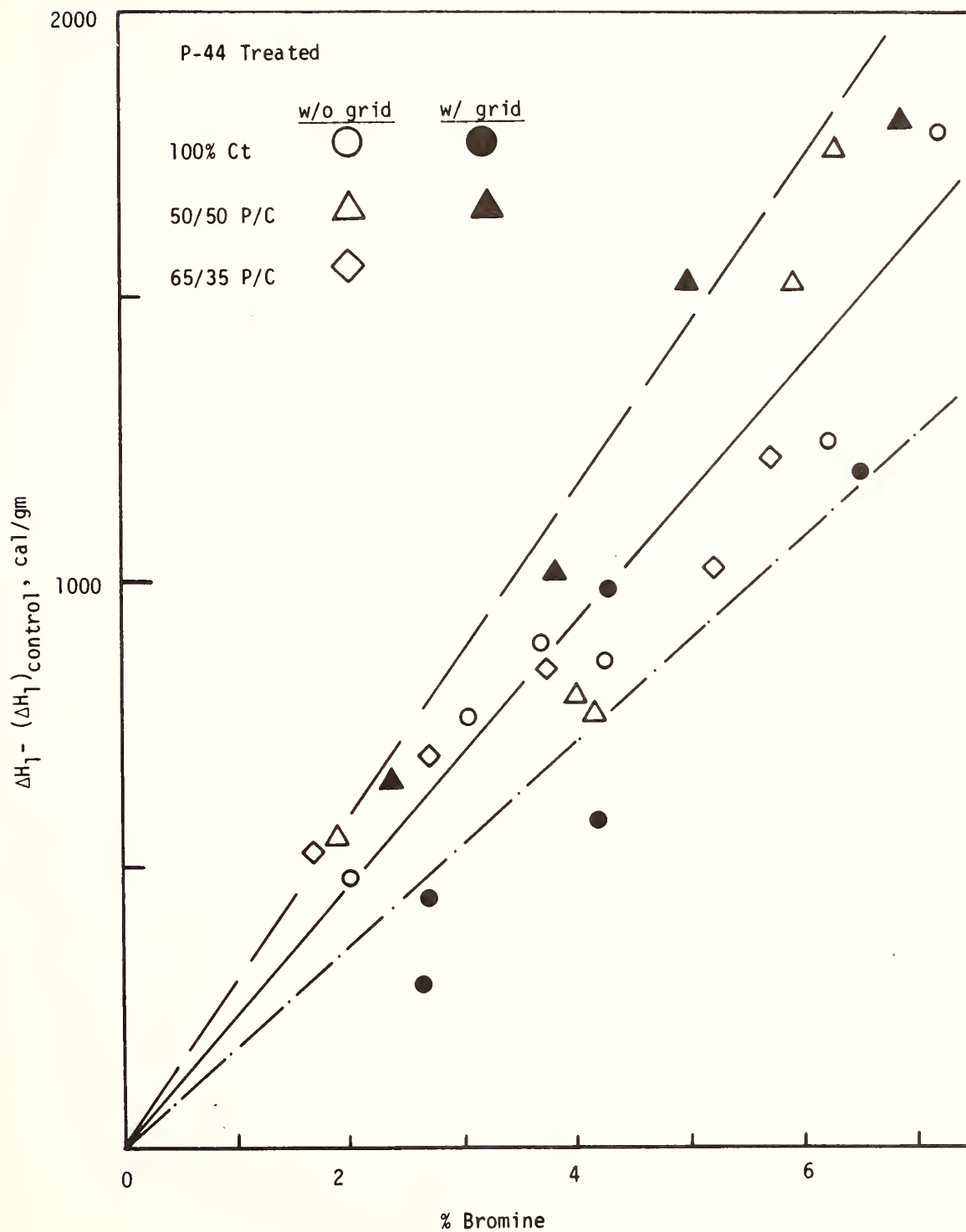


FIGURE 35. Net Heat Reduction of P-44 treated fabrics.

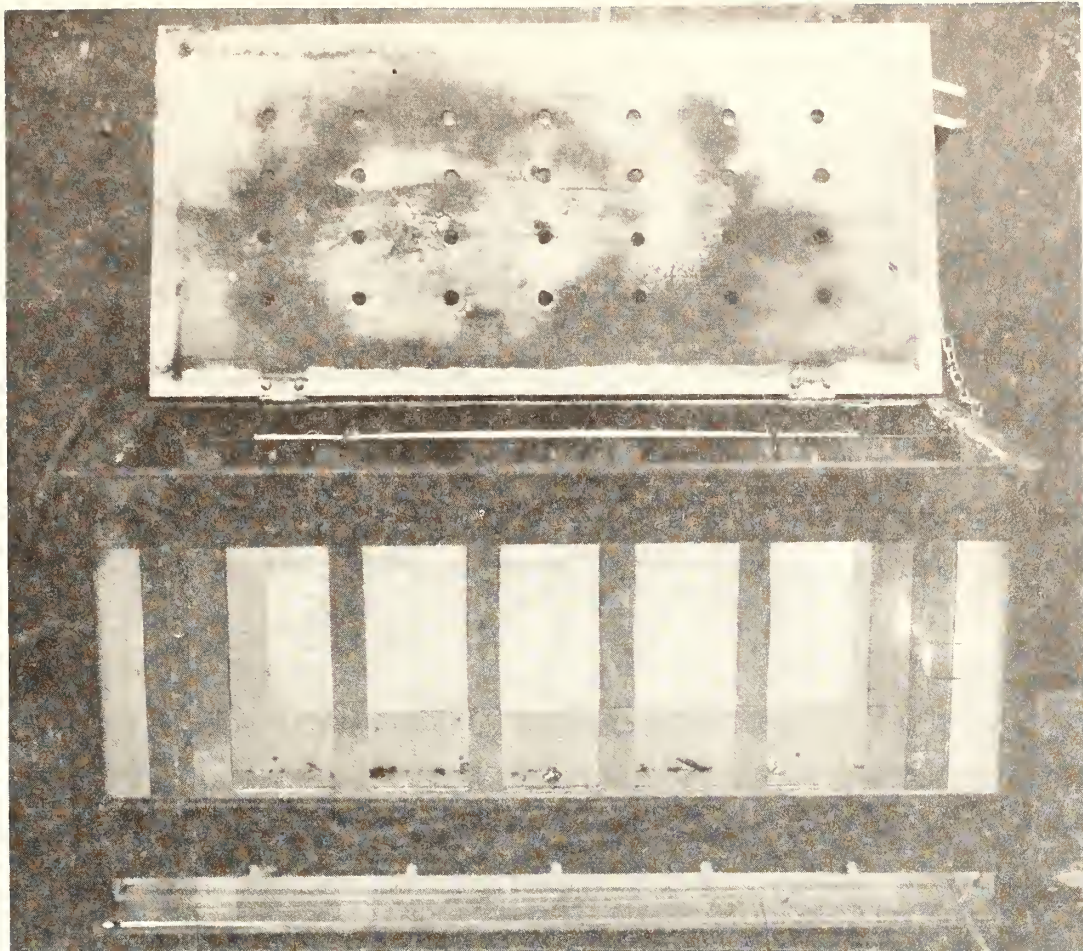
support provided by the grid. However, for 100% cotton, this difference consistently increases with additional bromine content in the fabric.

3. Correlation of Test Methods

A major area of concern in the testing program has been that involving the lack of correlation between the calorimetric data and the results of burning tests such as a vertical test (FF-5), the MAFT, or the subjective 45° angle test. While those fabrics which would not burn in the isoperibol calorimeter always were found to pass FF-5, the reverse is frequently not true. Many samples were found to perform well in FF-5 but burned completely in the isoperibol calorimeter with the evolution of relatively large amounts of heat. It would appear that these discrepancies result primarily from the very severe ignition conditions employed in the isoperibol technique. A study of the ignition behavior of flame retardant blend fabrics was therefore undertaken.

A small ignition chamber was designed and constructed to study the effect of ignition time and the difference between edge and surface ignition. This is shown in Figure 36. The ignition source chosen for the chamber was a 1" propane flame extending from the tip of a 22 gauge hypodermic needle. This design should result in ignition conditions somewhat similar to those proposed for use in the MAFT.

To test the chamber design and the reproducibility of the results obtainable with the device, a sequence of 12 blend fabrics was tested. These represented treatments with diammonium phosphate at two levels, the vinylchloridevinylbromide copolymer P(VBr/VCl) at two levels, and Pyrovatex[®] CP (with no resin). All of the samples were exposed to edge and surface ignition for 1, 3, 5, 7 and 12 seconds. The results are given in Table IX. As the data clearly show, there was little difference between edge and surface ignition within this small sampling of flame retardants. It does appear, however, that in the case of the totally condensed-phase active diammonium phosphate, sur-



(a) Sample Mounted for Edge Ignition.



(b) Sample Mounted for Surface Ignition.

TABLE IX

CHAR LENGTH IN CM AS A FUNCTION OF MODE OF IGNITION AND EXPOSURE TIME
ETIP 50/50 POLYESTER/COTTON

FR weight fraction	1 sec	3 sec	5 sec	7 sec	12 sec
$(\text{NH}_4)_2\text{HPO}_4$					
.208 \pm .006 BI ⁽¹⁾	.8 \pm .5	3.1 \pm .5	3.9 \pm .7	5.4 \pm .6	6.2
SI ⁽²⁾	.3 \pm .4	3.0 \pm .2	4.2 \pm .2	5.3 \pm .2	7.0
.117 \pm .005 BI	1.1 \pm .4	3.5 \pm .9	5.7 \pm .5	7.0 \pm .4	7.2
Pyrovatex ^(R) CP (no resin)					
.246 \pm .033 BI	.4 \pm .1	(3)	(3)	8.3 \pm .3	8.2
SI	.1 \pm .1	3.2 \pm .6	5.6 \pm 1.2	(3)	(3)
PVBr/PVCl					
.338 \pm .005 BI	.9 \pm .5	(3)	(3)	(3)	10.9
SI	.8 \pm .3	3.5 \pm .3	(3)	(3)	(3)
.216 \pm .007 BI	(3)	(4)	(4)	(4)	(4)
SI	1.0 \pm .0	3.3	.2	(4)	(4)

(1) Bottom Edge Ignition (3) One or more out of 6 samples burned entire length

(2) Surface Ignition (4) All six samples burned entire length

face ignition is slightly more severe; whereas the reverse is true of the vaporphase active P(VBr/VCl). While the char length reproducibility was found to be excellent for the DAP samples and the second set of VBr/VCl copolymer fabrics, some difficulties were encountered with those fabrics which tended to exhibit borderline burning characteristics. This was not surprising considering the complex nature of the ignition process.

On the basis of these preliminary trials it would seem that once a large enough data base is accumulated this test should provide valuable information concerning the mechanism of flame retardation. As a further example of the type of information available, some additional ignition exposure data for several fabrics treated with selected THPC precondensate finishes at various levels are presented in Table X.

In an attempt to establish direct correlations, calorimetric data and MAFT test results on some 40 fabrics have been obtained (mushroom data courtesy of NBS). These fabrics included both natural and synthetic fibers, with and without flame retardant treatments. Both the calorimetric and the MAFT data are tabulated in Table XI and XII. The calorimetric data are shown in terms of both the heat release, ΔH_1 , and the heat release per unit area, $-Q_1$. The latter parameter takes in account the effect of the fabric weight. Both values, $-Q_1$ and $-\Delta H_1$, were plotted vs. mushroom results, as shown in Figures 37 and 38, respectively.

Figure 37 shows that there is no direct correlation between $-Q_1$ and the mushroom. Furthermore, there is no clear-cut value of $-Q_1$, which corresponds to a passing margin in the MAFT, $0.10 \text{ cal/cm}^2\text{-sec}$. In addition, the data in Figure 37 indicate that MAFT results are relatively insensitive to difference in fabric weight, i.e., fabrics of same fiber type tend to have similar results, regardless of their differences in fabric weight. A plot of $-\Delta H_1$ vs MAFT results, as shown in Figure 38, also shows no direct correlation between the two values. However, a cut-off value of 1800 cal/gm for $-\Delta H_1$ can be chosen, where no fabric with $-\Delta H_1$ less than this value has failed the MAFT. Although, there are a few fabrics with $-\Delta H_1$ larger than

TABLE X
CHAR LENGTH AS A FUNCTION OF EXPOSURE TIME FOR ETIP 50/50
POLYESTER/COTTON WITH SEVERAL PRECONDENSATE BASED FINISHES

Finish, wt. %	Exposure time, bottom ignition			
	3 sec	5 sec	7 sec	12 sec
THPC/MeNH ₂				
.188	2.5cm	4.5cm	7.4cm	8.1cm
.154	3.0cm	5.2cm	8.3cm	8.6cm
.129	BEL	8.3cm	9.0cm	9.4cm
THPOH/MCC-100 ^(R)				
.229	2.7cm	6.5cm	7.5cm	6.8cm
.179	BEL	10.1cm	10.6cm	11.0cm
.131	BEL	BEL	BEL	BEL
THPC Acrylic				
.190	4.0cm	8.8cm	8.6cm	8.4cm
.252	4.4cm	7.3cm	7.5cm	7.3cm
Pyrovatex 3762 ^(R) (1)				
>.250				
THPC/MCC-100 ^(R) (1)				
>.250	2.8cm		10.0cm	8.6cm
THPC/Pyrovatex 4013 ⁽¹⁾				
>.250	2.9cm		6.9cm	8.2cm
THPC/Diamine ⁽¹⁾				
>.250	3.5cm		6.8cm	8.6cm
(1) Pass FF-5 (initial)				

TABLE XI
CALORIMETRIC AND MUSHROOM DATA OF SOME SELECTED FABRICS

Fabric	wt. gm/cm ²	-ΔH ₁ , cal/gm	-Q ₁ , cal/cm ²	Mushroom, cal/cm ² -sec
Cotton	10.8	3334	36.0	.38
Cotton (flannel)	12.5	3334	41.7	.11
Cotton (terry)	25.8	3334	86.0	.30
50/50 PET/CT(ETIP)	14.9	2942	37.0	.37
65/35 PET/CT	9.5	2846	27.3	.26
65/35 PET/CT	18.3	2846	52.1	.35
65/35 PET/CT	24.1	2846	68.6	.34
Wool	11.9	2206	26.3	.16
Acetate	8.1	3289	26.6	.11
Acetate	9.5	3289	31.2	.20
Acetate	15.9	3289	52.3	.22
80/20 Acetate/Nylon	9.2	3879	35.7	.13
Acrylic	17.3	4118	86.0	.35

TABLE XII
CALORIMETRIC AND MUSHROOM DATA OF F.R. TREATED FABRICS

Flame Retardant	wt. gm/cm ²	-ΔH ₁ , cal/gm	-Q ₁ , cal/cm ²	Mushroom cal/cm ² -sec
COTTON				
Fyrol 76 ^(R)	11.7	2170	27.6	.19
Fyrol 76 ^(R)	11.7	FTB*	----	.01
Fyrol 76 ^(R)	27.4	1973	47.7	.23
THPOH-NH ₃	11.7	1682	19.7	.01
THPOH-NH ₃	11.7	1746	20.4	.01
35/65 PET/CT				
Fyrol 76 ^(R)	13.2	2254	29.8	.15
Fyrol 76 ^(R)	13.2	2222	29.3	.15
Fyrol 76 ^(R)	13.2	2217	29.3	.01
THPOH-NH ₃	13.2	2202	29.3	.18
THPOH-NH ₃	13.2	1942	25.6	.01
THPOH-NH ₃	13.2	1901	25.1	.01
50/50 PET/CT				
Fyrol 76 ^(R)	23.9	2244	47.2	.17
Fyrol 76 ^(R)	23.9	2255	47.7	.13
Fyrol 76 ^(R)	23.9	2236	48.8	.11
THPOH-NH ₃	23.9	2225	42.9	.13
THPC/MCS 100/200/ 300 ^(R) (ETIP)	14.9	1911	28.5	.20
"	14.9	1842	27.4	.01
"	14.9	1778	25.4	.04 (.10)
50/50 PET/RAYON				
Fyrol 76 ^(R)	10.1	2339	26.3	.18
THPOH-NH ₃	10.1	2168	22.5	.21
THPOH-NH ₃	10.1	2268	22.9	.05
THPOH-NH ₃	10.1	2098	21.2	.05
65/35 PET/CT				
Fyrol 76 ^(R)	8.7	2189	20.5	.11
Fyrol 76 ^(R)	8.7	2338	22.1	.09
Fyrol 76 ^(R)	8.7	2261	19.7	.07
THPOH-NH ₃	8.7	2134	19.2	.11
THPOH-NH ₃	8.7	2070	19.1	.10
THPOH-NH ₃	8.7	2036	17.7	.07

*Fail to burn

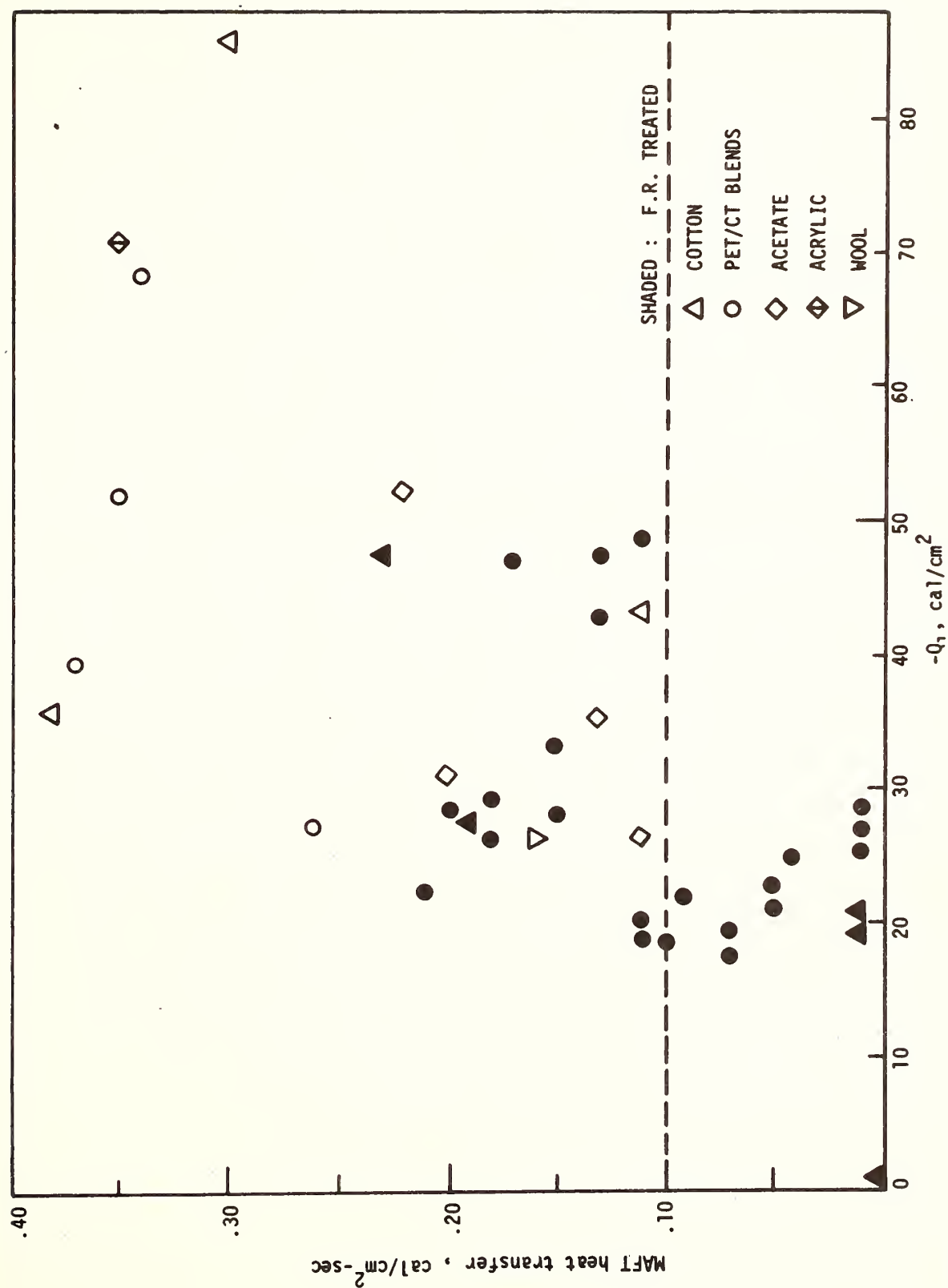


FIGURE 37. MAFT heat transfer as a function of fabric heat release per unit area.

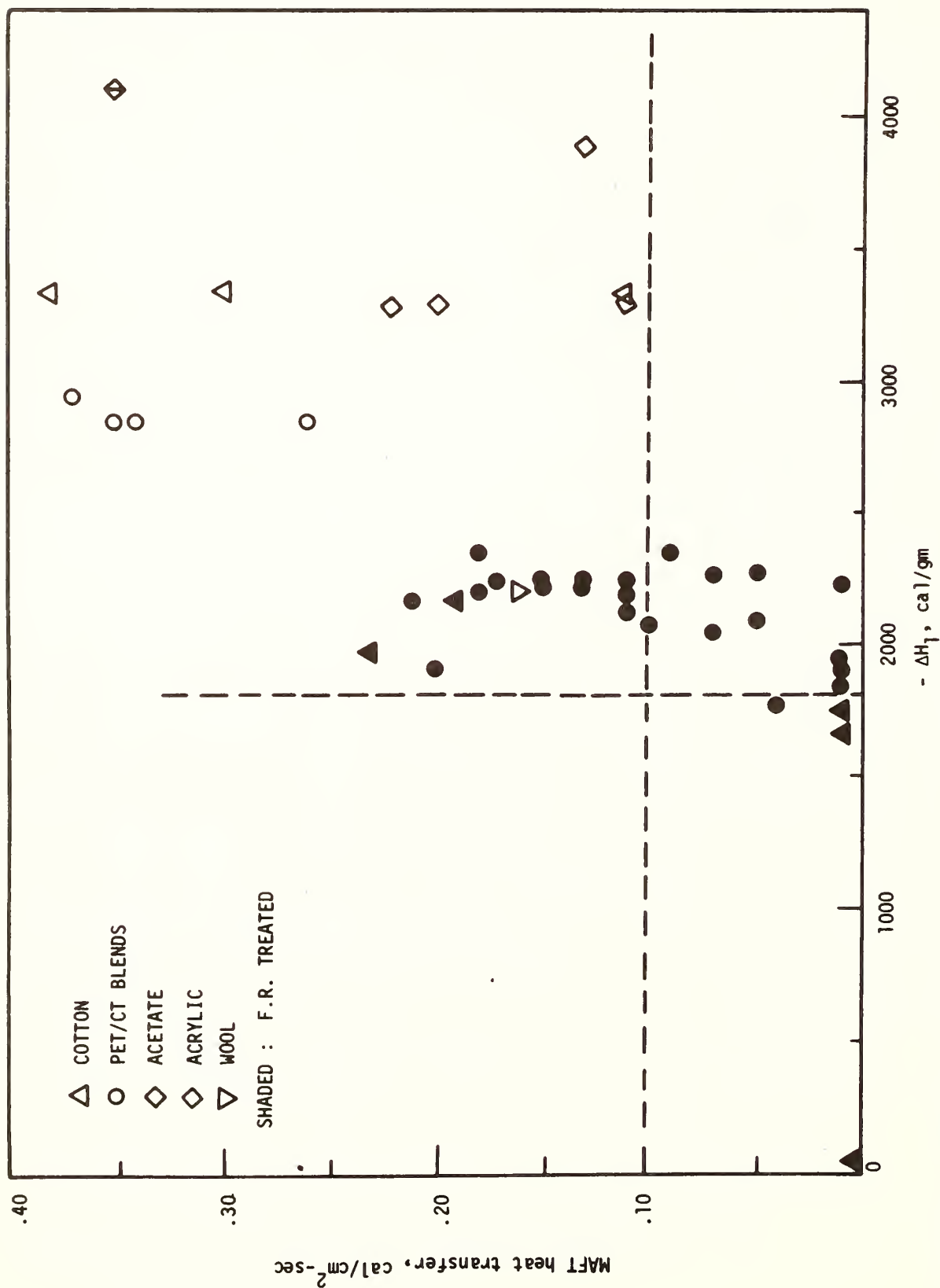


FIGURE 38. MAFT heat transfer as a function of fabric heat release.

1800 cal/gm that passed the MAFT, the value of 1800 cal/gm is chosen as the cut-off value which assures a Class I rating on the MAFT.

An attempt was also made to evaluate the possibilities of a direct correlation between OI and various vertical tests. Data comparing OI and FF 3-71 char lengths are given in Table XIII. On the basis of these data it would seem that there is a point near OI=30 above which 100% cotton fabrics treated with phosphonium salt finishes usually have good behavior but there is no point at which the samples can be assured of passing FF 3-71.

Tables XIV, XV and XVI present similar data for three commercial finishes using a modified vertical test run on samples conditioned at 65% RH. Under these conditions it would appear that the fabrics also begin to exhibit borderline flammability behavior at about OI=29-30. Again there seems to be little correlation between OI and char length above this value.

Using the same procedure on 100% PET fabrics gave quite different results as shown by the data in Table XVII. All of these samples, including the control, displayed small char lengths because of their melt-drip characteristics. A similar insensitivity of the vertical test was encountered with the polyester knits shown in Table XVIII. These data also show little dependence of flammability on fabric construction. This points out the problems of using vertical tests as a measure of flammability with thermoplastics.

TABLE XIII

CHAR LENGTH (FF-3) vs OI ON 100% COTTON FABRICS

Flame Retardant	OI	Char Length (in.)
Control	19.2	BEL
Pyroset TKS (R)	32.5	1.5
Pyroset TKS (R)	31.8	5.5
Pyroset TKS (R)	29.7	BEL
THPC (R) urea/Na ₂ HPO ₄	35.0	2.0
THPC (R) urea/Na ₂ HPO ₄	34.4	BEL
THPOH-NH ₃	33.7	1.0
THPOH-NH ₃	33.7	1.3
THPOH-NH ₃	33.7	1.5
THPOH-NH ₃	33.7	2.8
THPOH-NH ₃	34.4	2.5
THPOH-NH ₃	34.6	2.1
THPOH-amide	33.5	1.4
THPOH-amide	35.0	1.2

TABLE XIV

FLAMMABILITY OF FABRICS TREATED WITH FYROL ^(R)76

Fabric (cotton/polyester)	% Add-on	OI	Char Yield	Char Length Conditioned
50/50	18.7	26.0	20%	10 in
70/30 Cotton/PET	19.9	24.7	18%	10 in
<u>Controls</u>				
50/50	-----	20.0	21%	10 in
70/30 Cotton/PET	-----	19.2	---	10 in

TABLE XV
FLAMMABILITY OF FABRICS TREATED WITH PYROSET TK-115

Fabric (cotton/polyester)	% Add-on	OI	Char Yield	Char Length Conditioned
50/50	--	29.7	23.5%	9.3 in
50/50	19.5	29.7	25.3%	10 in
70/30	26.4	32.5	29%	2.4 in
70/30	22.4	32.1	24.5%	4.0 in

TABLE XVI
FLAMMABILITY OF FABRICS TREATED WITH FR P-44^(R)

Fabric (cotton/polyester)	% Add-on	OI	Char Yield	Char Length Conditioned
50/50	---	31.8	3%	1.9 in
50/50	---	29.7	6%	2.1 in
50/50	30.8	29.0	5%	2.7 in
50/50	22.0	28.6	3%	4.2 in
70/30	---	34.1	3%	1.9 in
70/30	---	31.8	5%	-----
70/30	26.7	30.9	3%	2.2 in
70/30	21.3	28.6	4%	5.5 in

TABLE XVII

FLAMMABILITY OF FLAME RETARDANT TREATED POLYESTER FABRICS

	% Add-on	OI	Char Length Conditioned
Control	1.3	23.3	1.8 in
Flame Snub Intermix ^(R)	8.8	26.0	1.5 in
Chargard FR 989 ^(R)	12.1	30.5	1.2 in
Glo-Tard PE-10 ^(R)	6.6	30.1	1.0 in
Tanatard DN-2 ^(R)	7.5	31.1	1.3 in.
Firemaster 200 ^(R)	8.6	32.1	1.0 in
Beaunit's Lab emulsion	7.5	31.1	1.7 in

TABLE XVIII
FLAMMABILITY BEHAVIOR OF POLYESTER SINGLE KNITS TREATED WITH 15%
TANATARD PN-2

Sample	OI	Char Length, in.
150 Den. Textured PET TWILL	38.0	2.5
150 Den. Textured PET LACOSTE	35.0	2.6
150 Den. Textured PET CREPE	33.1	2.4
150 Den. Textured PET BROKEN RIB	33.5	1.8
150 Den. Textured PET CORD	35.6	2.6
150 Den. Textured PET ARGYLE	37.8	3.1
150 Den. Textured PET RIB	31.1	2.5
18/1 Spun PET JERSEY	33.5	2.1
18/1 Spun PET JERSEY	33.1	1.7
18/1 Spun PET RIB	31.4	1.0
150 Den. Textured PET PONTE DI ROMA	36.4	1.7
150 Den. Textured PET TWILL	35.9	1.9

POLYESTER

1. Basic Factors Affecting PET Flammability

1.a. Pyrolysis of Untreated Polyester:

In order to develop the type of fundamental information on the thermal reactions of polyester and treated polyester which seemed to be required for the design of flame retardants which would be efficient on polyester, and indepth fundamental study was initiated at the Polytechnic Institute of New York under the direction of Dr. Eli M. Pearce. The objective of the early studies was to investigate the relationship between PET structure parameters and its thermal degradation and flammability. A series of specially designed polyesters was prepared by the research group at American Enka Company under the direction of Dr. Alan Meierhoefer. In all, 11 samples were made with systematic variations in molecular weight, carboxy end group concentration, and diethylene glycol concentration (DEG) as shown in Table XIX. Complete characterization of the polymers was carried out by American Enka. TGA analysis of the polyester samples was conducted on a Mettler No. 13 thermal analyzer using a deep dish-shaped aluminum crucible and weight losses were obtained in the range of 60-80%. This weight loss was considerably less than expected. In order to verify the results, one sample was analyzed in a nitrogen atmosphere and the rate of heating was changed from 6° per minute to 15° per minute. There was no change in the observed weight loss. Subsequently, the other samples were analyzed on a DuPont 950 thermal analyzer using an open boat-shaped crucible and heated in circulating air. Losses under these conditions were considerably higher, and generally in the neighborhood of 90%.

In view of these differences in weight loss, one polyester sample was analyzed on the Mettler equipment using a flat dish platinum crucible. The rate of heating varied from 6° to 20° per minute. Weight loss was found to be 87% indicating that more degradation had occur-

TABLE XIX
POLYESTER SAMPLES PREPARED FOR FLAMMABILITY STUDIES

Polymer Number	I V	COOH Meg/kg	COOCH ₃ Meg/kg ³	Mn ppm	Sb ppm
Z-422-1P	.47	8	1.00	3	274
Z-423-1P	.64	11	0.80	3	263
Z-424-1P	.54	12	2.06	3	250
Z-425-2P	.74	16	0.94	3	296
T-443-1P	.57	42	1.63	3	307
T-444-1P	.63	12	1.63	3	278
T-451-1P	.64	28	1.75	3	258
T-453-1P	.56	30	1.75	3	278
T-461-1P	.71	16	1.96	3	254
T-461-1P-D	.61	70	1.96	3	254
T-461-2P	.64	23	0.93	3	263

red. The anomalous result with the deep dish procedure and observation that char initially forms on the surface in this procedure may indicate diffusion controlled processes which relate to the presence of surface char. However, such an interpretation is made less attractive by a subsequent series of experiments in which PET was degraded under TGA conditions at various heating rates. Heating at 6° and 25° per minute produced weight losses of 89-91% while 50° per minute produced a weight loss of 82-88%. These results are summarized in Figure 39.

In a concurrent set of thermal experiments, the polyester samples were analyzed in both TGA and DTA modes on Mettler thermal analyzer in an attempt to determine transition points. In these experiments, however, the glass transition points were not obtainable because of poor instrument sensitivity. Melting points were found to vary from 250° to 270° and are tabulated in Table XX. More systematic investigation with more sensitive equipment would be required before meaningful interpretation of these parameters could be accomplished.

As a measure of polymer flammability, the series of polyester samples was subjected to oxygen index evaluation in powder form. This was accomplished in an inverted porcelain crucible. When the sample was heated for ignition with a propane flame, the sample fused into a flat lump in the center of the lid; the top of the lump then melted and subsequently discolored. At this point, ignition occurred with the production of a sooty, but steady flame. After increasing the nitrogen gas pressure, the flame fluttered and then extinguished. At this point, an oxygen index was determined. Every sample was replicated 3 times and an average OI value calculated (Table XXI). Correlation of the oxygen index with {COOH}, DEG content, intrinsic viscosity, metal content, and weight loss was attempted. Only {COOH} was found to have any relation to OI. The log OI was observed to be linearly proportional to the reciprocal of log {COOH} (Figure 40). A log-log plot was necessary to remove the considerable scatter in the data. Although these results are ambiguous, they have been interpreted by the PINY group as indicating that the flammability of the polymer sample tends to increase with increasing concentration of

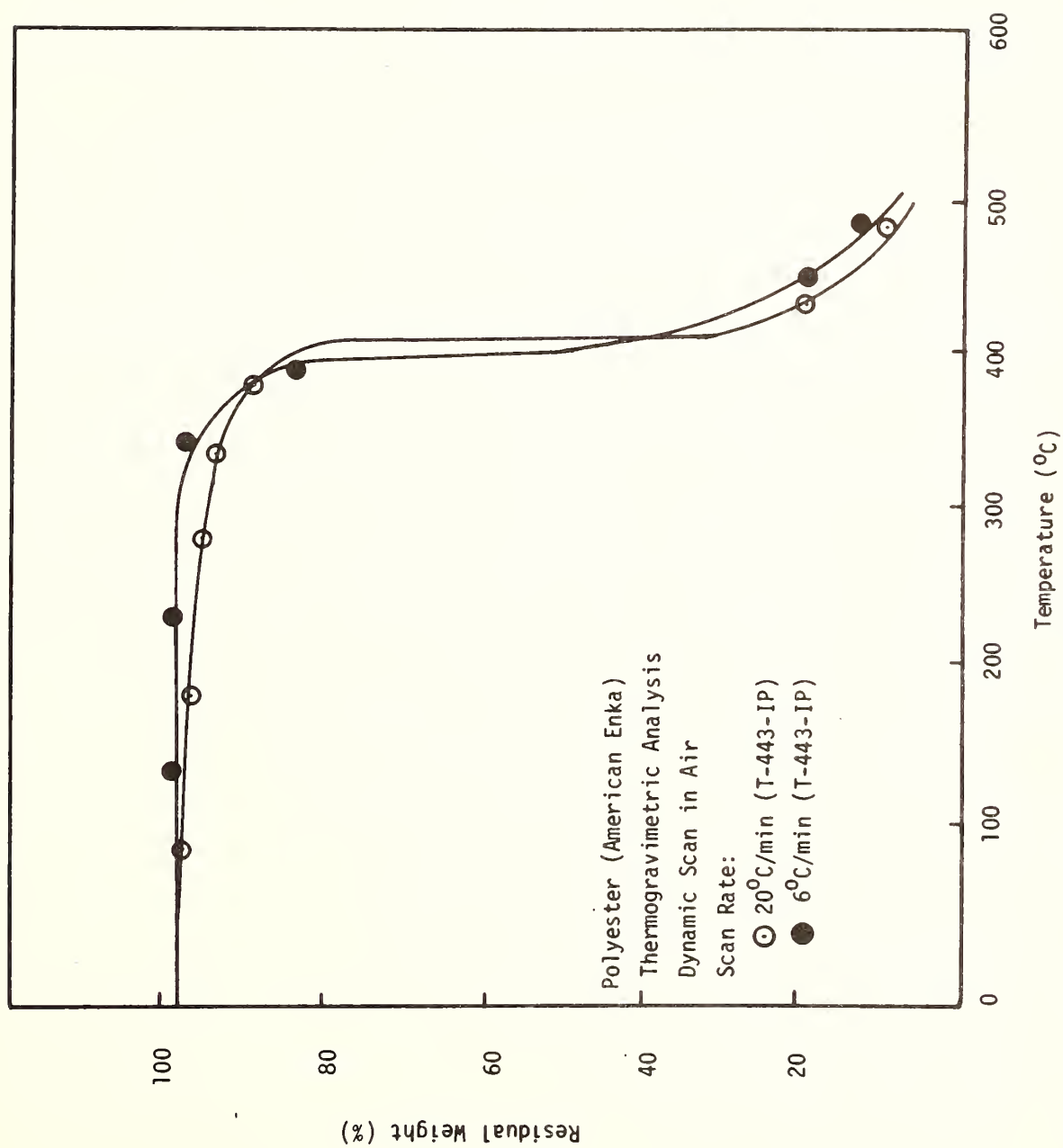


FIGURE 39. Effect of scan rate on the TGA of PET in air.

TABLE XX
THERMOGRAVIMETRIC WEIGHT LOSS AND MELTING POINT OF POLYESTERS

Polymer Number	Weight Loss (at 500°C)	Melting Point** °C
Z-422-1P	82*	270
Z-423-1P	80*	260
Z-424-1P	76*	270
Z-425-1P	93 ⁰	255
T-443-1P	90 ⁰	250-270
T-444-1P	89 ⁰	---
T-451-1P	90 ⁰	252
T-453-1P	91 ⁰	255
T-461-1P	89 ⁰	260
T-461-1P-D	88.5 ⁰	252
T-461-2P	90 ⁰	249

*Run on Mettler Analyzer in deep dish crucible

⁰Run on DuPont 950^(R) TGA in boat shape crucible

**DTA on Mettler^(R) Thermo Analyzer at heating rate of 15°C/min

TABLE XXI

OXYGEN INDEX OF POLYESTERS

Polymer Number	<u>Oxygen Index %</u>			Average
	I	II	III	
Z-422-1P	18.1	17.9	18.4	18.1
Z-423-1P	18.4	20.23	20.23	19.6
Z-424-1P	22.42	21.31	21.43	21.7
Z-425-2P	19.8	18.1	18.1	18.6
Z-443-1P	16.6	17.2	16.6	16.8
Z-444-1P	16.6	16.6	17.2	16.8
T-451-1P	16.4	16.6	16.6	16.5
T-453-1P	16.6	16.6	17.27	16.8
T-461-1P	16.6	16.6	17.2	16.8
T-461-1P-D	16.4	16.25	16.25	16.3
T-461-2P	16.6	17.27	17.27	17.0

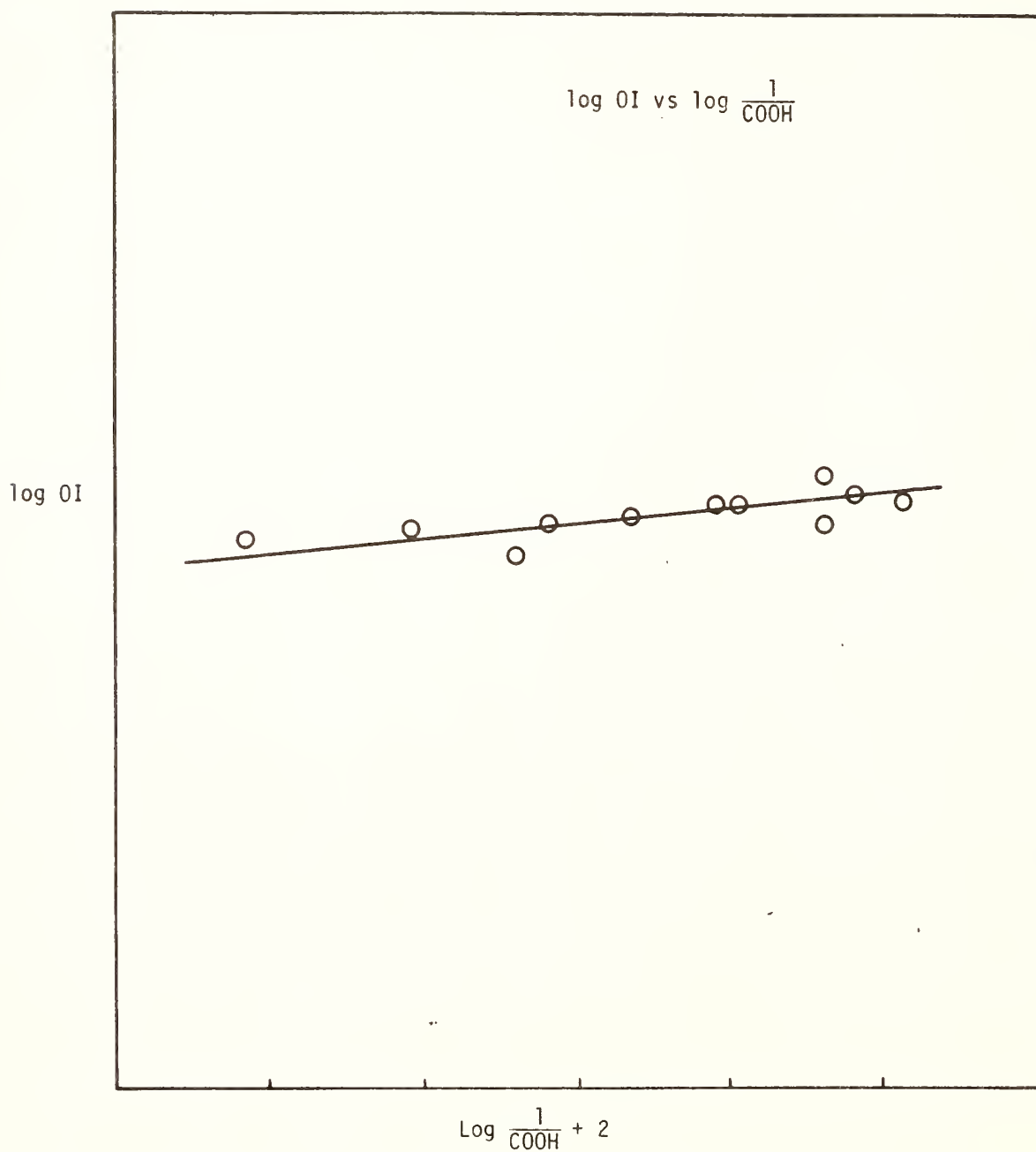


FIGURE 40. Log OI as a function of $\text{Log } \frac{1}{\text{COOH}} + 2$ for PET.

carboxy end groups. This would be consistent with carboxy catalyzed degradation reactions such as ester hydrolysis. It has also been noted by several workers that the concentration of carboxy groups tends to increase during the process of PET thermolysis (60). Thus, the effect of carboxy on flammability could become increasingly important as the degradation continues. The dependency upon the initial carboxy content should be small, as indicated, because of the effect, and the occurrence of the random cyclic ester pyrolysis mechanism, which may become dominant during degradation, and which does not appear to be affected by the presence of other compositional features.

1.b. Effect of Bromine on Polyester Flammability:

In addition to the studies of the pyrolysis of pure PET, the PINY project had the added objective of determining the effect of mode of incorporation of flame retardants on the properties of PET. Both bromine and phosphorus based systems were studied.

A series of polyester copolymers and homopolymer mixture had been prepared previously by Yoon, Liepins and Pearce at RTI. These polymer systems contained brominated flame retardants at a level sufficient to give incorporation of 4-8% bromine. The copolymers were prepared from PET and the bishydroxyethyl ether of tetrabromobisphenol-A. Homopolymer mixtures contained polyester and the tetrabromobisphenol-A as an additive. When these samples were analyzed thermogravimetrically up to 500°C in an air atmosphere, using a 15° per minute heating rate, the weight loss of the copolymers was found to decrease as the bromine content increased. The results with the polymer mixtures were more erratic in relation to the bromine content. They are summarized in Table XXII.

These samples were also evaluated in terms of oxygen index. The copolymers containing 4% bromine melted completely and later started burning on the top, whereas samples containing 6-8% bromine melted partially before igniting. The OI increased with increasing bromine content. All of the homopolymer mixtures partially melted before

TABLE XXII
THERMOGRAVIMETRIC WEIGHT LOSS ANALYSIS AND OXYGEN INDEX OF
COPOLYMERS AND HOMOPOLYMER MIXTURES

Sample Number	Sample Type	Bromine Content %	Weight Loss* % (500°C)	OI %
C-4	Copolymer	4.03	81.25	15.7
C-6	Copolymer	6.28	79.07	17.3
C-8	Copolymer	7.62	73.72	18.8
M-4	Mixture	4.00	79.07	17.2
M-6	Mixture	6.00	74.04	22.2
M-8	Mixture	8.00	77.16	23.9
PET	-----	None	90.00	15.6
Mixture of Bis(2,3-dibromo- propyl ether) of TBBPA		4.00	76.00	21.5
		8.00	75.00	21.7

*15°C/min. Heating Rate.

burning and the OI values increased with increasing bromine content. The value of the OI was comparatively higher with the mixtures than in the case of the copolymers. These results are also summarized in Table XXII. Since these experiments indicated that, in the case of bis(hydroxyethyl)tetrabromobisphenol-A, the incorporation of the flame retardant into the polymer backbone reduced the efficiency of the retardant relative to that which it exhibited when present in mixtures with PET homopolymer. To explain this, it was proposed that the bis(hydroxyethyl)ester was capable of undergoing a facile pyrolysis with the liberation of ethylene oxide and the free bromo phenol functions. The bromo phenol could then undergo its well known reaction with the elimination of hydrogen bromide. However, when the mixture was incorporated into the polymer backbone, this mode of decomposition was inhibited resulting in less efficient liberation of the bromine retardant. In an effort to substantiate this hypothesis, a mixture of PET with bis(2,3-dibromopropyl)tetrabromobisphenol-A was prepared and evaluated by oxygen index. As shown in Table XXII, the OI values obtained on these samples were higher than those obtained from any of the previously studied copolymers. However, a comparison of these results with those obtained on the bis(hydroxyethyl)tetrabromobisphenol-A was considerably more confusing. The bromopropyl ether appears to be more efficient at a bromine content of 4% and less efficient at a content of 8%. More surprisingly, the effect of the bromopropyl ether appears to be essentially independent of the bromine content within this limited range. The reasons for this behavior are not at all clear.

In order to better understand the nature of the activity exhibited by bromine compounds on polyester and blends containing polyester, a study of model organobromine reagents was initiated at Clemson. These studies were frustrated by repeated failures to achieve reasonable add-on levels of the model compounds. Only bromo phenols were found to give sufficient add-on when padded from a 20% solution. An application of 2,4,6-tribromophenol at a level of approximately 12% was found to raise the oxygen index of 100% polyester to 27.5. Similar applications

to 50/50 blends yielded less efficient retardancy. The tribromophenol produced an oxygen index of 21.5 at an add-on of 16.4% on the blend. The reason for this difference in efficiencies is not clear since the bromo compound presumably acts entirely as a vapor phase retardant and thus should be insensitive to the chemical nature of the substrate. It was felt, however, that this might be related to the problem of distribution of the flame retardant among the cotton and polyester portions of the sample. In order to study the effect of distribution in greater detail, samples of 65/35 and 50/50 blend fabrics were treated with tris(dibromopropyl)phosphate as a model system. Following application and drying, portions of the treated fabric were subjected to oxygen index evaluation. The remainder of the samples were heated at temperatures above 130° to effect migration of the phosphate into the polyester in a manner analagous to thermosol treatment. Portions of these samples were then evaluated by oxygen index also. The results of these tests also indicated no difference in flame retardancy as a function of location of the bromophosphate in the polyester. The remaining portion of the samples were extracted with perchlorethylene and evaluated for flammability. This, of course, reduced the total level of phosphorus and bromine in the system as it extracted the majority of the material from cellulose. Oxygen index values, however, were found to be essentially the same as those obtained on the previous samples containing corresponding levels of retardant. These data tend to indicate that the effectiveness of a retardant such as tris(dibromopropyl)phosphate, which is presumed to act primarily in the vapor phase, is a function only of the amount of retardant present and not significantly dependent upon the location of the retardant in the various fibers.

There is, however, some evidence that other organobromine derivatives may have a small, but measureable, effect in the condensed phase in both cellulosic and polyester fibers. Thermal analysis has been carried out on polyester films containing approximately 20 weight percent of a series of bromine containing flame retardants. These included polyvinylbromide, octabromobiphenyl and decabromodiphenyl-

oxide. Samples of DuPont's type 900F Dacron[®] containing tetrabromobisphenol-A were also analyzed. It appears that all of the bromo compounds exhibit a small catalytic effect on the polyester degradation. However, the amount of residue remaining at 500° does not appear to be significantly altered by the presence of the retardants.

Pyrolysis-gas chromatography (GC) studies indicated a similar small interaction. Samples were prepared as films containing 20% of the flame retardant. In addition, films of pure polyester and of Dacron[®] 900F were cast for comparison purposes. Small specimens were cut from each of the films and weighed carefully. They were then pyrolyzed at 800°C for 200 msec into a gas chromatograph with the column temperature programed from 70°C to 190°C at a rate of 5° per minute. The column was then held at 190°C for ten minutes to complete the run. The results of these studies are shown in Figures 41 and 42. The development of a new peak in the flame retardant films is clearly demonstrated. This peak was eluted from the column at a temperature of 156°C. The fact that this new peak did not result from pyrolysis of the flame retardants is clearly shown in Figure 41 since the peak was not observable in the pyrolysis chromatograms obtained on the pure retardants. Polyvinylbromide has two similar peaks, but they were eluted from the column before the FR/PET compound. It is interesting to note that Dacron[®] 900F, which contains a brominated comonomer, also has this newly detected pyrolysis product. Although the compound exists in differing amounts, it is present in all of the flame retardant polyesters studied.

Attempts were made to identify this new pyrolysis product and to determine its significance in the overall process of flammability and flame retardation, but no conclusive results could be obtained. The elution time of the material suggests a brominated ring structure. The formation of this material, however, may be quite incidental as the amount of low molecular weight products given off during the pyrolysis of the flame retardant samples was not significantly affected by any of the retardants. Polyvinylbromide actually seemed to increase the amount of low molecular weight gases released.

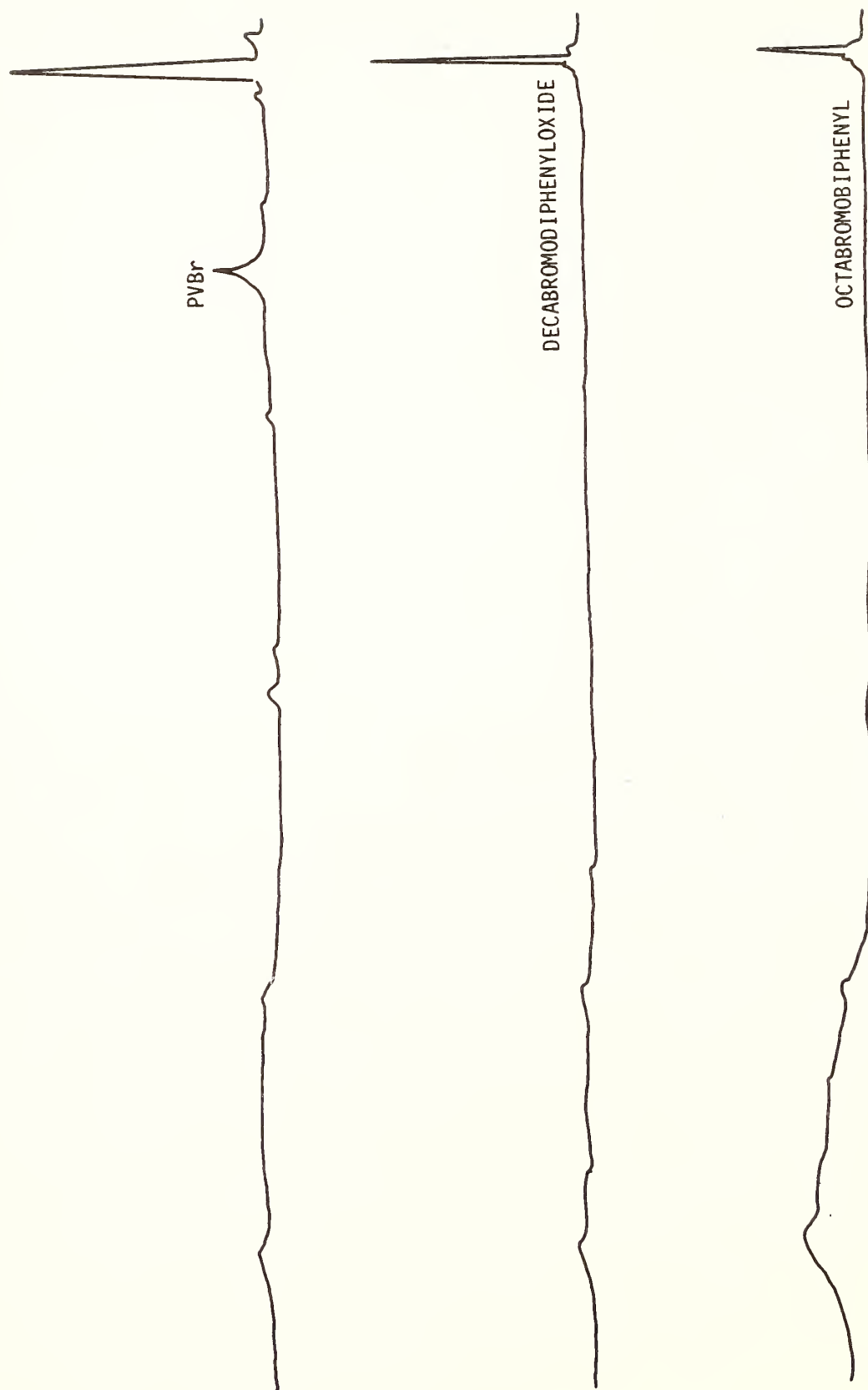


FIGURE 41. GC pyrolysis of bromine containing flame retardants.

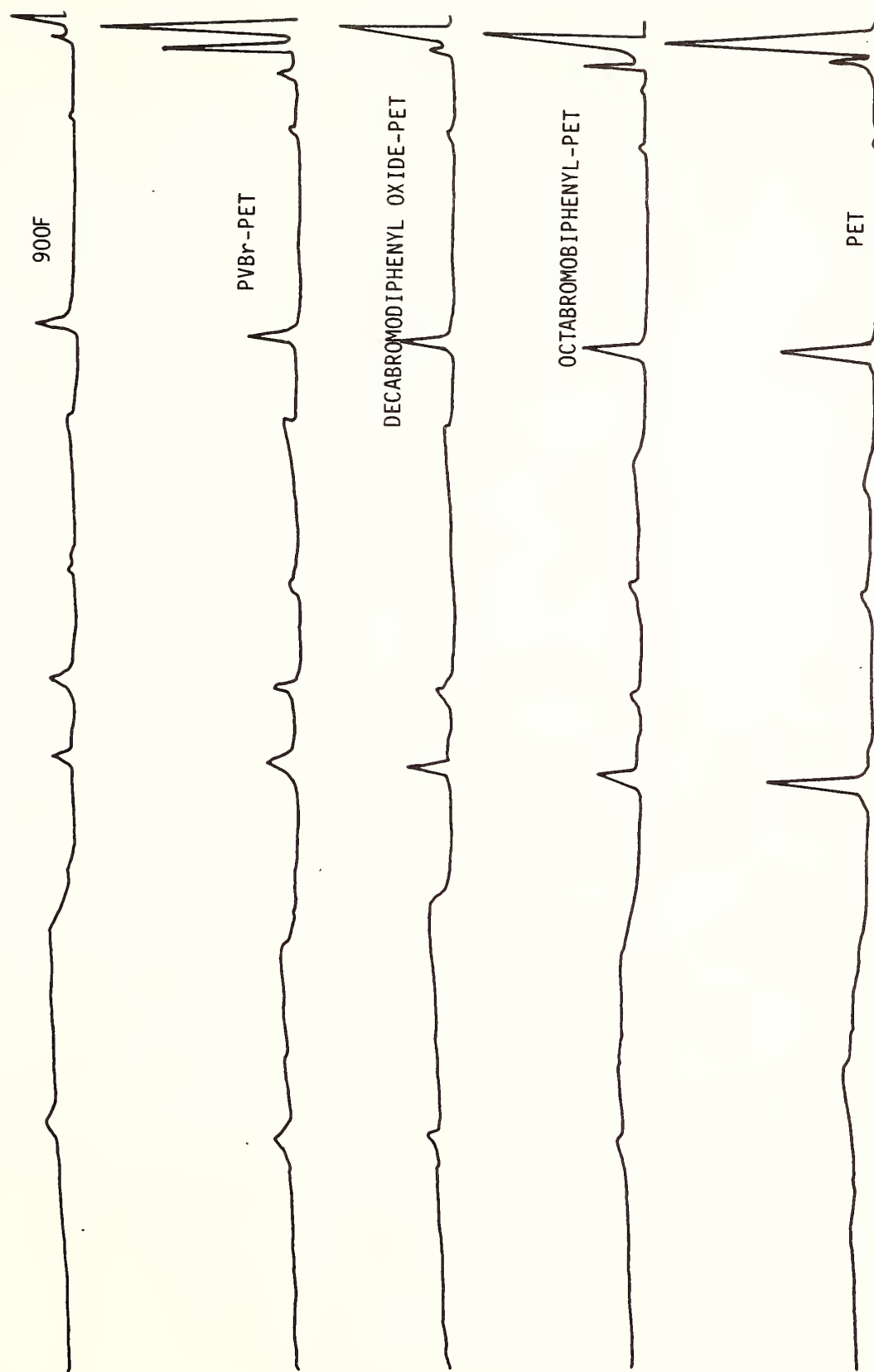


FIGURE 42. GC pyrolysis of PET films containing bromine flame retardants.

Since all these studies indicated that the predominate flame retardant effects of organobromine compounds could be described in terms of their vapor phase activity, it seemed that one of the controlling factors for FR efficiency should be their thermal stabilities. Because aromatic bromine compounds, in general, degrade at a higher temperature than aliphatic compounds, they should be more effective as fire retardants for PET. Hence a study was initiated to measure the efficiency of a series of aromatic and aliphatic bromine compounds on polyester fabric in an attempt to relate their effectiveness as fire retardants to their chemical structure.

Of the compounds studied, PVBr and poly(2,3-dibromopropyl acrylate){P(DBPA)} contained bromine atoms attached to aliphatic structures, while octabromobiphenyl (DBBP), decabromodiphenylene oxide (DBDPO), and TBBPA contained bromine attached to aromatic nuclei.

All fabric samples were treated from aqueous emulsions of flame retardants, with the exception of TBBPA, which was padded from acetone solution. The DBBP and DBDPO were applied with an acrylic latex, Dur-O-Cryl[®] XWC, as a binder. The TBBPA treated samples were topped with the same acrylic latex in an attempt to insure that the test results were not influenced by differences in physical behavior of the treated samples.

Fabric flammability was measured by oxygen index and isoperibol calorimetry. The OI values were determined for treated PET samples containing increasing amounts of each of the fire retardants and are shown in Figure 43. Linear regression analysis of the data showed that the OI results from all of the samples fit on one line with a confidence level of $r = 0.97$. Thus the OI values appear to be dependent only on the amount of bromine in the fabric, regardless of which brominated compound was applied.

Contrary to the OI results, the isoperibol calorimeter measured significant differences in flame retardant efficiencies for the different bromine-containing compounds. The heat released by the treated samples when they burned in the calorimeter $(\Delta H_1)_S$ was subtracted from the heat released by the untreated PET control, $(\Delta H_1)_C$. This

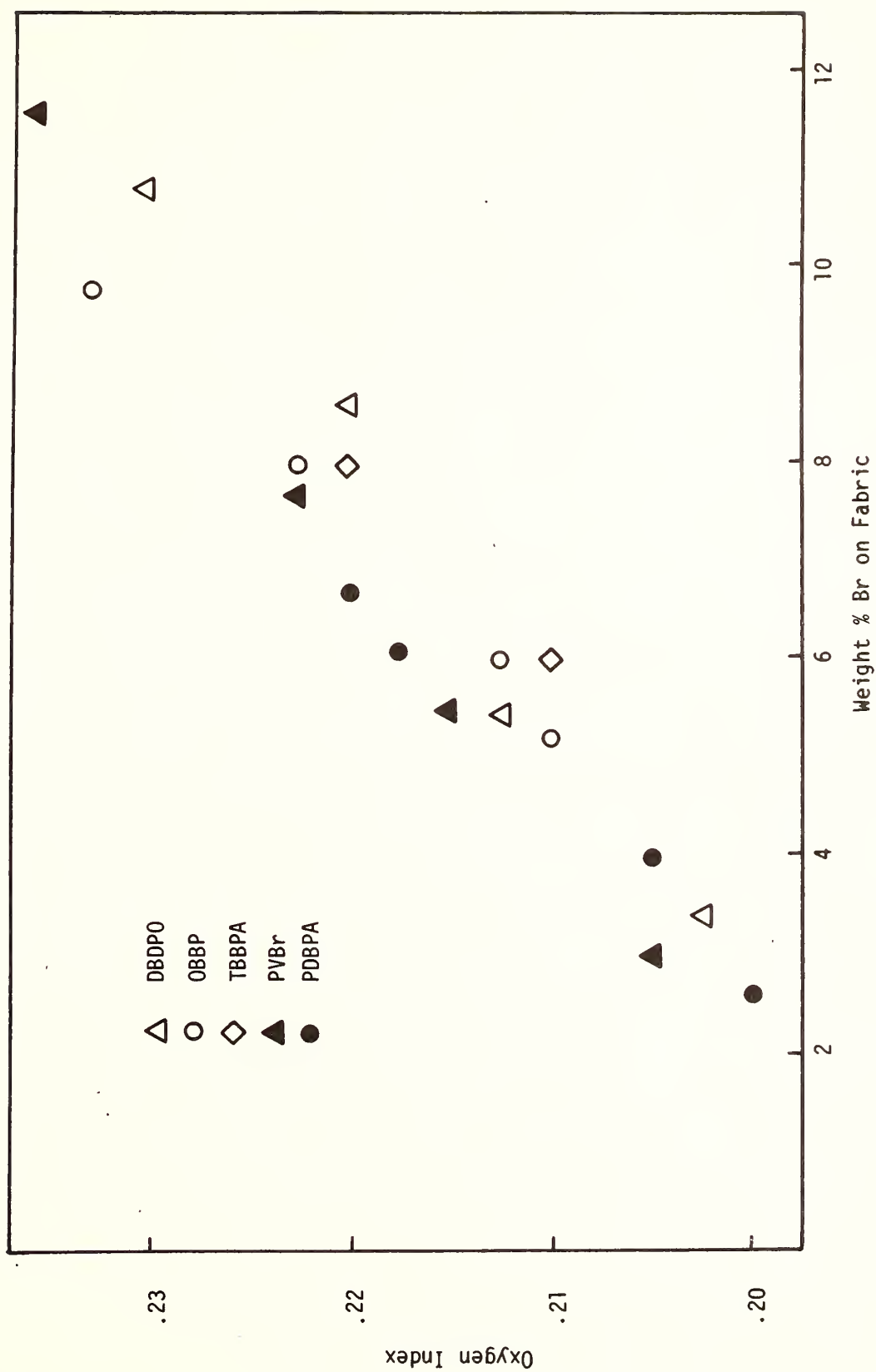


FIGURE 43. The relationship between OI values and weight % Br in PET fabrics treated with bromine fire retardants.

difference was plotted versus weight percent bromine in the fabric and is shown in Figure 44. The slope of the resulting lines gave the heat reduction per weight percent bromine in each of the fabric systems. This number indicated the relative efficiencies of the selected compounds as fire retardants on PET fabric. Table XXIII summarizes these efficiency data. The OBBP and DBDPO were shown to be the most efficient fire retardants tested, followed by TBBPA and P(DBPA), while PVBr was the least efficient.

The contradictions in OI and calorimetry results are probably a consequence of the configuration in which samples are burned in the two testing apparatuses. In the isoperibol calorimeter, samples are placed at a 45° angle and ignited from the bottom. Hot gases emerging from the flame front are swept upward over the fabric surface, ahead of the advancing combustion zone. This should increase the width of the polymer preheating zone, creating higher temperatures in the fabric at greater distances from the flame. Volatile flame retardants should have a greater chance of leaving the condensed phase ahead of the flame. Since escaping gases are swept upward by the air flow of the system, the volatile inhibiting species would not pass through the reaction zone. Hence the effectiveness of a thermally unstable flame retardant would be greatly reduced.

In contrast, OI samples are mounted vertically and ignited from the top. Combustion products escape upward away from the fabric surface, and are unable to transfer their heat to the fabric sample. The polymer preheating zone should be narrowed and occur closer to the advancing flame. Any gases evolved from the decomposing polymer would be released below the combustion zone, and their path of escape would carry them through the flame. This should decrease the importance of fire retardant volatility, and make the efficiency of a brominated fire retardant depend only on the amount of bromine it contains.

These factors should combine to make the isoperibol calorimeter more sensitive than the OI in detecting differences in fire retardant efficiency that result from flame retardant thermal stability. This was illustrated by test results from fabrics treated with PVBr. A

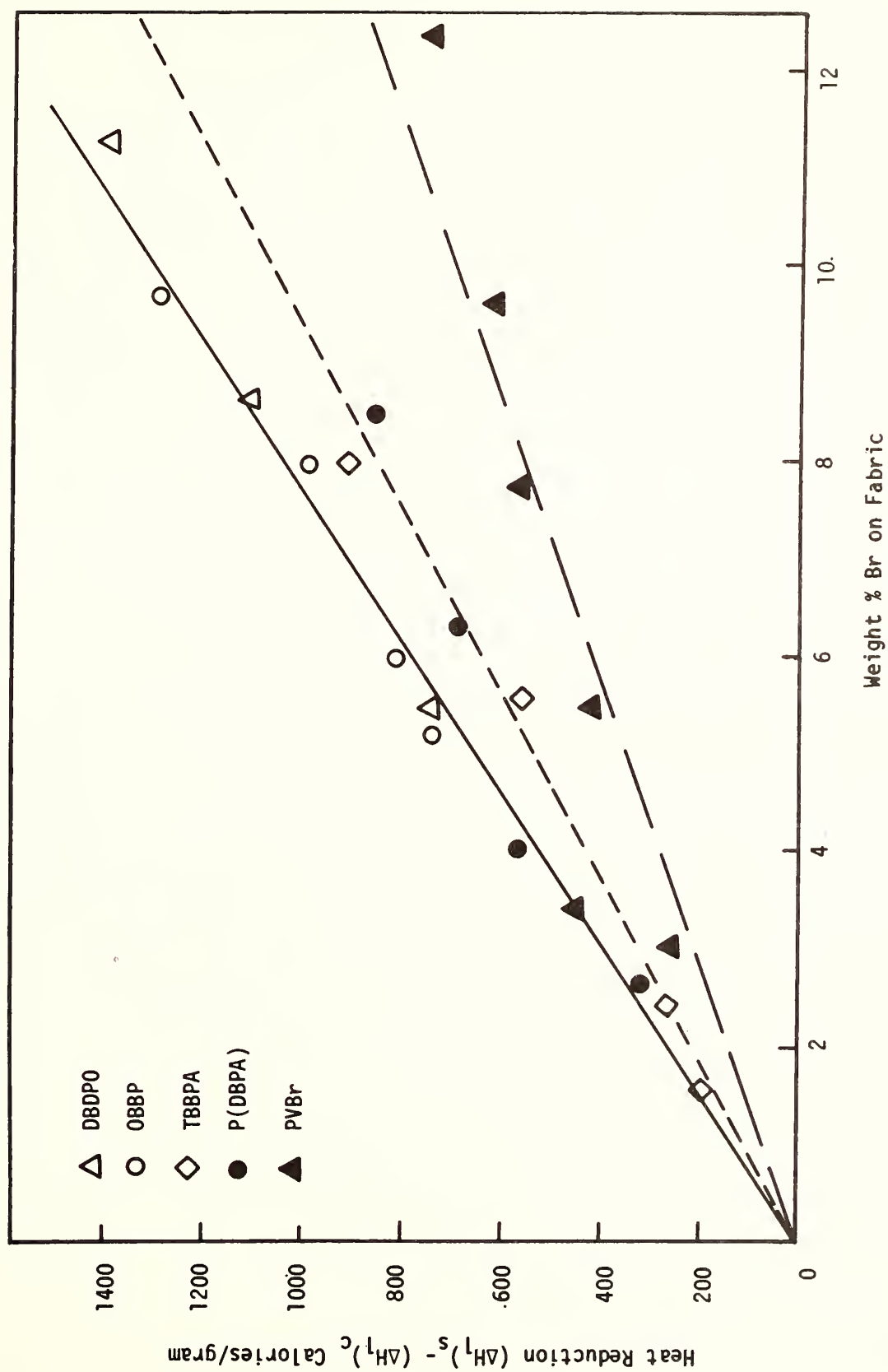


FIGURE 44. Heat reduction of burning PET fabrics treated with bromine fire retardants.

TABLE XXIII
SUMMARY OF LINEAR REGRESSION ANALYSIS
OF ISOPERIBOL CALORIMETRY RESULTS

Flame Retardant	Intercept	Heat Reduction cal/gr per % Br	Confidence Level, r
PVBr	81	55	0.98
P(DBPA)	65	97	0.96
TBBPA	20	107	0.99
DBDPO	34	122	1.00
OBPP	20	129	0.99

very effective flame inhibitor, HBr, is known to be released when PVBr decomposes. However, this evolution occurs at 175°C, which should make the effectiveness of PVBr sensitive to burning configuration. In the OI, PVBr was as effective as any other bromine compound treated, but its relative efficiency was greatly reduced when burned in the isoperibol calorimeter.

The low degradation temperature of PVBr is typical of many aliphatic bromine compounds. However, the calorimetric results showed that PDBPA exhibited fire retardant efficiency similar to TBBPA. This indicated that in PET the thermal stability of aliphatic PDBPA was also similar to that of aromatic TBBPA. These results preclude any specific statements as to the effectiveness of aliphatic bromine compounds versus aromatic compounds. However, the data suggest a general trend, supporting the assumption that aromatic compounds are more effective, possibly because they release their inhibiting species at higher temperatures, closer to the advancing flame front.

In an attempt to verify this interpretation an experimental procedure was designed to measure HBr evolution from fire retardants during pyrolysis.

TGA in conjunction with a Br⁻ specific ion electrode was used to monitor HBr evolution. Dacron[®] 900F and fabric samples treated with the organobromine compounds were heated at 10°C/min under nitrogen and air atmospheres to a maximum temperature of 500°C. The compounds flame retardant additives were pyrolyzed alone under the same conditions for comparative purposes. Pyrolysis gases from the TGA were passed through a beaker containing 50 ml of distilled water and the bromide ion concentration monitored. It was assumed that all Br⁻ absorbed came from HBr evolved from the pyrolyzing samples.

Table XXIV gives a summary of the total amount of bromide ion absorbed in the distilled water when the flame retardants and treated samples were pyrolyzed. R_{FR} is the ratio of bromine absorbed to bromine originally present for the pure fire retardant, and R_{FAB} the same ratio for treated fabric samples. The values reported are an average of at least three TGA experiments. There was no apparent difference

TABLE XXIV
HYDROGEN BROMIDE RELEASE OF BROMINE FIRE RETARDANTS

Flame Retardant	R_{FR}	R_{FAB}
PVBr	0.33	0.26
PDBPA	0.12	0.13
900F	----	0.12
TBBPA	0.033	0.092
DBDPO	0.002	0.027
OBBP	0.001	0.006

in bromide ion absorption or TGA curves when the pyrolysis atmosphere was changed from N_2 to air, indicating that oxygen was not involved in HBr evolution.

These results show that PVBr released the most HBr of the compounds studied with approximately 30% of the bromine initially present in the sample being absorbed by the distilled water. HBr evolution occurred over a temperature range of 175⁰-250⁰C. Since PVBr is known to release practically all of its bromine as HBr, it was taken as a reference to which the other compounds were compared.

P(DBPA) pyrolysis resulted in 12% of its bromine being absorbed as HBr, with absorption occurring in the temperature range of 250-315⁰C. This represented only 30-40% as much HBr evolution as PVBr, indicating that significant amounts of bromine were released in other forms. The TGA of P(DBPA) suggest that HBr evolution is occurring simultaneously with polymer molecular fragmentation. This could result in the volatilization of bromine containing polymer fragments, resulting in a decrease in the relative amount of HBr produced.

The three aromatic flame retardants behaved differently than PVBr and P(DBPA). Only TBBPA released any significant HBr, and it was only 10% of the amount released by PVBr. During the thermal analysis of the aromatic compounds, white powders were deposited on the glass TGA cover and the inside of the glass bubbler. The bubbler clogged completely during two of the TBBPA tests. Small amounts of these powders were collected and infrared analysis showed the deposits to be undecomposed flame retardants in all three cases. Apparently the aromatic bromine fire retardants tested are entering the vapor phase as intact, undecomposed molecules. TBBPA volatilized at 200-275⁰C, DBBP at 250-340⁰C, and DBDPO at 275-370⁰C.

The evolution of HBr resulting from the pyrolysis of treated fabric samples and Dacron[®] 900F was also studied. Comparison of these thermograms shows good agreement between the amount of condensed phase reactivity detected in the pyrolysis-G.C. experiments and the amount of HBr released during the time of polymer thermal degradation. This supports the conjecture of reactions occurring between vinyl groups

present during PET degradation and escaping HBr.

The treated fabric thermograms also showed that PVBr again produced more HBr than any of the other fire retardants. Nearly all of the HBr produced by PVBr was released before PET degradation began. This would be consistent with the interpretation that in the upward burning configurations the majority of the HBr is released before the flame front arrives, greatly reducing the effectiveness of PVBr as a flame retardant.

P(DBPA) in the presence of PET released the same relative amount of HBr as P(DBPA) pyrolyzed alone, indicating no significant interaction between the decomposing polymers. In contrast, TBBPA treated polyester fabric produced relatively larger quantities of HBr than TBBPA alone. Dacron[®] 900F released a similar fraction of its bromine as HBr compared to the topically treated fabric samples. This indicated that the increase in HBr production might have been caused by TBBPA being physically held in the polymer system, allowing it to reach higher temperatures where decomposition could occur. Evidently a volatilization process is competing with the thermal decomposition processes. The polymer melt could have decreased the rate of TBBPA escape and allowed more of the compound to decompose and release HBr. At the elevated temperatures of the polymer melt, it is conceivable that TBBPA is reacting with PET through transesterification, which would result in TBBPA being held in the condensed phase. This would allow the topically treated samples to exhibit similar behavior to the Dacron[®] 900F, where the TBBPA is part of the polymer backbone. These data indicate that bromine flame retardant efficiency cannot be explained simply in terms of HBr release.

This conclusion was further demonstrated by the OBBP and DBDPO fabric samples. These samples were the most efficiently retarded, but they released very small amounts of HBr. OBBP produced practically no HBr, while DBDPO produced only a small amount. The TGA's suggest that OBBP and DBDPO were probably released into the flame as intact molecules by volatilizing out of the fabric. Compound decomposition must occur in the flame itself, releasing the bromine in the location

where it can have the greatest inhibitory effect.

It is interesting to note that a proposed mechanism for bromine-antimony synergism calls for the reaction of HBr with antimony oxide in the condensed phase of the polymer system (60). Other work has shown this synergistic effect to be a real one by examining the White Chemical FR P-44[®] (antimony oxide-DBDPO). However, the TGA studies have shown that DBDPO produces negligible HBr when heated to 500°C by itself, and only a small amount of HBr when heated to 500°C with polyester. The large increase in flame retardant efficiency by the addition of antimony oxide thus cannot be attributed to its reacting with such a small amount of HBr. This suggests that reactions between DBDPO and antimony oxide are occurring by a yet unknown mechanism.

The comparative thermal stabilities of the studied bromine fire retardants is given in Table XXV. As mentioned it was noted that TBBPA volatilizes at higher temperatures in the presence of PET. With this in mind, a good correlation can be drawn between the temperature of the maximum rate of weight loss of the fire retardants and their relative efficiency in PET. This indicates that, for the compounds in this study, the temperature at which the bromine-containing species leaves the substrate is more important than the chemical nature of either the volatilizing species or the compound present in the substrate.

These results imply that in PET systems containing only bromine as the flame retardant, the most efficient system would be one that released its bromine-containing species at the same time that the polymer released its flammable gases. This should place the bromine directly into the flame reaction zone where its resulting inhibition would be most efficient.

1.c. Effect of Phosphorus on Polyester Flammability:

In addition to the studies centering on bromine compounds, efforts were expended in the area of phosphorus chemistry. The team at PINY has synthesized a series of phosphorus containing materials to be used in a similar series of investigations. All of these are based on

TABLE XXV
THERMAL ANALYSIS OF BROMINE FIRE RETARDANTS

Fire Retardant	Temperature Range of Weight Loss, °C	Temperature of Maximum Rate of Weight Loss, °C
PVBr	175-225	200-205
PDBPA	250-305	295-300
TBBPA	200-275	270-275
OBPP	250-340	330-335
DBDPO	275-370	360

phenylphosphonyl dichloride, as commercially obtained from Stauffer Chemical Company and included phenylphosphonyl di(methyl benzoate) and phenylphosphonyl di(p-methyl oxybenzoate).

The 1:1 molar copolymer was prepared by the reaction of bis(2-hydroxyethyl)terephthalate and phenylphosphonyl di(p-methyloxybenzoate) by heating at 160° for 8 hours at 0.1 mm pressure. It contained 4.5 mole% phosphorus (theory for 1:1 copolymer - 4.8%). The copolymer contained 4.5 mole% phosphorus (calc. 4.8%), was pale brown and has a 0.78 inherent viscosity at 30°C. This sample could be spun manually and had a T_g of 42°C and a melting point of 191°C. The sample was evaluated by OI and weight loss was evaluated by TGA. The OI values was about 30.8 and the weight loss was around 84% at 500°C.

The 1:1 molar copolymer obtained by the reaction of bis-(2-hydroxyethyl)terephthalate and phenylphosphonyl di(p-methyl benzoate) was prepared in a similar fashion heating for 8 hours at 200°C under 0.1 mm pressure. The sample contained about 5 mole% of phosphours, was dark brown and had a $(\eta)_{inh}$ of 1.3. It could be spun manually. The polymer had a T_g of 42°C and a melting point of 172°C. The OI value was 29.0 and the weight loss by TGA was 72%.

These copolymer samples were compared to two additive systems. The phenylphosphoyl di(p-methyl benzoate) monomer and triphenylphosphine oxide, respectively, were added to PET as additives. The concentration of phosphorus was 5 mole% in order to compare the flammability effects directly with the phosphorus containing copolymers. Triphenylphosphine oxide had previously been shown to act in the vapor phase while reducing the flammability of PET (12).

The monomer and triphenylphosphine oxide (TPPO) samples were first studied alone by TGA to understand their potential behavior as additives. The data indicate that triphenylphosphine oxide essentially is degraded and volatilized 100% at 500°C. Some oxidation of TPPO occurs and is indicated by an initial early small gain in weight, whereas phenylphosphonyl di(p-methyl benzoate) degraded from the beginning and showed a weight loss of about 90% at 500°C.

PET samples were melt blended with phenylphosphonyl di(p-methyl

benzoate) monomer and TPP0, respectively, and then were studied by TGA and the oxygen index. PET melt blended with phenylphosphonyl di(p-methyl benzoate) degraded after 220°C and decomposed after 290°C. The weight loss was 27% at 500°C and gave an OI of 29. Ester interchange reactions are rapid and thus could account for the very similar results with the copolymer. PET melt blended with TPP0 showed an early weight loss, with a final weight of 96% at 500°C as compared to PET itself which has a weight loss of 90% at 500°C. The OI was 24.5, which is higher than the 17.0 value for unmodified polyester sample. These results suggest that TPP0 apparently acts in vapor phase (12) while phenylphosphonyl di(p-methyl benzoate) appears to operate primarily in the condensed phase. A simple powder blend of PET and the phenylphosphonyl di(p-methyl benzoate) also had an OI of 26.5.

A summary of the weight loss and oxygen index data is shown in Table XXVI. The contrast between the vapor phase action of triphenyl phosphine oxide and the condensed phase action of phenylphosphonyl di(p-methyl benzoate) was notable. It would also appear that a non-reactive phosphorus additive (TPP0) which operates in the vapor phase was a less efficient flame retardant for PET than those which are reactive or can be copolymerized and also may act in the condensed phase.

A further indication that phosphorus may be capable of some condensed phase activity on PET can be found in the results of a study at Clemson. As shown in Table XXVII, application of diammonium phosphate to 100% PET fabric imparted significant flame resistance. Since DAP is essentially nonvolatile under the FF 5-74 test conditions, its action is presumed to be restricted to the condensed phase. However, the interpretation of these results is complicated by the effects of the increased levels of moisture expected to be present in the DAP treated fabrics. This is demonstrated by the observation that samples of the fabric containing 3.5% P burned readily when stitched with 3 fiberglass threads and oven dried before testing. A similar series of glass supported samples conditioned in the normal laboratory atmosphere exhibited borderline flame resistance with a failure rate of

TABLE XXVI
P CONTAINING ADDITIVES AND/OR COMONOMERS IN PET
(~5 mole% P)

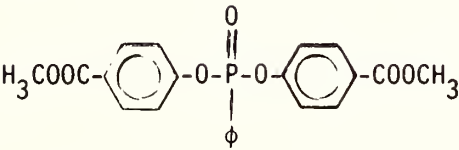
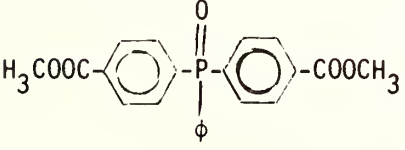
<u>Structure</u>	<u>Type</u>	<u>% Weight loss, (500°C)</u>	<u>OI</u>
PET	homopolymer	90	17.0
PET + 	copolymer	84	30.8
PET + 	copolymer	72	29.0
	additive	75	29.0
PET + $\phi_3\text{P=O}$	additive	96	24.5

TABLE XXVII

Flammability of Diammonium Phosphate Treated Polyester

<u>% Add-on</u>	<u>% P (theoretical)</u>	<u>FF 5-74 (Avg. Char Length)</u>
26.3	4.78	4/4 (1.1 in.)
17.8	3.47	4/4 (1.6 in.)*

* 4.7 seconds afterflame

50% in FF 5-74.

1.d. Role of Condensed Phase Oxidation in PET Flammability:

In most of the previous studies it has been assumed that the effects of condensed phase oxidation were insignificant in the polyester combustion process. However, in view of recent work by Stuetz and others (61), it was felt that an attempt should be made to either confirm or disprove this experimentally.

Samples of PET were therefore examined by TGA in both the presence and absence of oxygen. The differential curves showed little reproducibility but in any event the curves found in inert environments were different than those found in 20% oxygen. Since at higher heating rates the decomposition processes merge to form a single peak, it is not possible to determine the importance of heating rate on the processes taking place.

On the basis of these results the temperature range chosen for the isothermal studies was 350°C to 420°C. The lower temperature was the point at which loss begins to take place. The upper limit was the approximate temperature at which the rate of weight loss was observed to be a maximum.

To test the effect of sample surface area on the rate, the following three configurations of PET were examined: chip, fiber, and fiber Wiley milled to a 40 mesh. If the oxidation processes were strongly dependent on the surface area one would expect the rates to increase in order of powder > fiber > chip. The decompositions were carried out at 356°C in atmospheres of 0, 5, 12, and 20% oxygen, and the rate constants determined assuming a first-order rate dependence. The values as shown in Table XXVIII did not indicate any effect of the various configurations on this order or magnitude. For the purpose of homogeneity of samples the Wiley milled fiber was employed in the remainder of this work.

For the remainder of the PET studies five temperatures were used: 334, 356, 369, 387, and 407°C. Table XXVIII contains the rate constants

TABLE XXVIII

COMPARISON OF RATE CONSTANTS, k, FOR DIFFERENTIAL

CONFIGURATIONS OF PET IN VARYING OXYGEN

ENVIRONMENTS AT 356° C

$\% O_2$	CHIP $k(\text{min}^{-1})$	Fiber $k(\text{min}^{-1})$	Powder $k(\text{min}^{-1})$
0	5.4×10^{-3}	6.1×10^{-3}	6.4×10^{-3}
5	8.6×10^{-3}	6.9×10^{-3}	7.7×10^{-3}
12	5.9×10^{-3}	7.5×10^{-3}	8.0×10^{-3}
20	1.4×10^{-2}	1.2×10^{-2}	1.3×10^{-2}

found at these temperatures with varying oxygen concentrations in the environment. The order was found to be pseudo first-order, although the weight loss at the lowest temperature appeared to be zero order. At higher temperatures, however, the kinetics seemed to be approaching second order. A possible explanation for this may be that the reaction appeared to be zero order at the lower temperatures because the rate of weight loss was slow. Thus over the time span used, it could appear linear. The onset of charring at higher temperatures could also cause an apparent deviation from first-order kinetics.

Ideally, isothermal TGA can be used to discriminate between several processes that may result in weight loss. For PET it is difficult to completely differentiate between pyrolysis and oxidation, since the weight loss occurs over a relatively narrow temperature range and both processes appear to occur simultaneously. As the data in Table XXIX show, the value for the PET decomposition rate constant in the presence of a 20% oxygen environment is twice that in 100% nitrogen at 334°C. At higher temperatures less of an increase of rate in the presence of oxygen was observed. This possibly indicates that pyrolysis takes place faster than oxidation at higher temperatures where more energy is available.

The dependence of activation energies on the amount of oxygen present during the degradation clearly shows that an increase in oxygen content catalyzes the weight loss. From the observed doubling of the rate constant it can be shown that the oxidative processes are actually occurring faster than the nonoxidative process. Theoretically, if the rate of decomposition is pseudo first-order the rate is given by the equation:

$$\text{Rate} = k_1(\text{PET})$$

where k_1 = rate constant for decomposition

(PET) = weight of PET in the TGA experiment

Experimentally in a nitrogen environment the rate is found to be expressed given by:

$$\text{Rate } N_2 = k_{py}(\text{PET})$$

TABLE XXIX

THE EFFECT OF OXYGEN ON THE DECOMPOSITION RATE, k , OF DACRON^a 54

POLY(ETHYLENE TEREPHTHALATE)

% O ₂	334° C		356° C		369° C	
	$k(\text{min}^{-1})$	Std. Dev. ^a	$k(\text{min}^{-1})$	Std. Dev. ^a	$k(\text{min}^{-1})$	Std. Dev. ^a
0	9.00×10^{-4}	0.18×10^{-4}	5.94×10^{-3}	0.4×10^{-3}	1.26×10^{-2}	0.01×10^{-2}
5	1.22×10^{-3}	0.08×10^{-3}	7.77×10^{-3}	0.1×10^{-3}	1.51×10^{-2}	0.02×10^{-1}
12	1.38×10^{-3}		7.93×10^{-3}	0.2×10^{-3}	1.74×10^{-2}	0.05×10^{-2}
20	1.99×10^{-3}	0.14×10^{-3}	1.26×10^{-2}	0.16×10^{-2}	2.45×10^{-2}	0.09×10^{-2}

% O ₂	387° C		407° C	
	$k(\text{min}^{-1})$	Std. Dev.	$k(\text{min}^{-1})$	Std. Dev.
0	2.86×10^{-2}	0.15×10^{-2}	9.92×10^{-2}	0.06×10^{-2}
5	3.76×10^{-2}	0.12×10^{-2}	1.05×10^{-1}	0.20×10^{-1}
12	4.83×10^{-2}	0.33×10^{-2}	1.26×10^{-1}	0.02×10^{-1}
20	5.26×10^{-2}	0.45×10^{-2}	1.53×10^{-1}	0.04×10^{-1}

^aStandard deviation of the mean k of at least three samples.

where k_{py} = rate constant for pyrolysis.

Therefore the theoretical rate constant, k_1 , is equal to the experimental rate constant k_{py} . When oxygen is introduced into the environment, oxidation occurs primarily at the surface so the theoretical rate of decomposition will consist of contributions from both decomposition routes. It would then be described by the equation:

$$\text{Rate}_{\text{Mix}} = k_{1\text{Mix}}(\text{PET}) = k_{py}(\text{PET}) + k_{O_2}(\text{PET})_{\text{surface}}$$

where k_{O_2} = rate constant for decomposition by oxidation.

If the rate constant doubles with the introduction of a 20% oxygen environment, $k_{1\text{Mix}} = 2k_{py}$, then the relation of k_{py} to k_{O_2} is given by:

$$k_{py}(\text{PET}) = k_{O_2}(\text{PET})_{\text{surface}}$$

which can be rearranged to:

$$\frac{k_{py}(\text{PET})}{(\text{PET})_{\text{surface}}} = k_{O_2}$$

Since the fraction $(\text{PET})/(\text{PET})_{\text{surface}}$ is clearly much larger than unity k_{O_2} is much larger than k_{py} .

The results at 387°C for PET in the form of Dacron[®] 54 were compared under the same environments to those from a deep dye PET from American Enka made by the introduction of an aliphatic diester comonomer. Since the deep dye polyester has a more open structure it would seem reasonable to assume that it would have the capacity to absorb more oxygen into its matrix than Dacron[®] 54. If it does absorb more oxygen one would expect an increase in the rate constants that were found for the PET under comparable conditions. The results in Table XXX show that the rate constants are higher in the case of the deep dye polyester than with normal PET in all the situations studied. However, the decomposition rate constants increased systematically by a factor of approximately 1.2 when the standard deviation from the mean was considered. This suggested that the increase in the rate constants was due to a feature present at the beginning of pyrolysis rather than

TABLE XXX

Comparison of the decomposition rate constants, k , for
Dacron[®] 54 and deep-dyeing PET

% O ₂	Dacron [®] 54	Deep-Dyeing PET	Std. Dev. ^a
	387° C k min ⁻¹	387° C k min ⁻¹	
0	2.86 x 10 ⁻²	3.53 x 10 ⁻²	0.13 x 10 ⁻²
5	3.76 x 10 ⁻²	5.25 x 10 ⁻²	0.43 x 10 ⁻²
12	4.83 x 10 ⁻²	5.51 x 10 ⁻²	0.39 x 10 ⁻²
20	5.25 x 10 ⁻²	5.60 x 10 ⁻²	0.22 x 10 ⁻²

^a Standard deviation of the mean k of at least three samples.

an increase in adsorption of oxygen during pyrolysis. This phenomenon could be the result of an increase in adsorption of oxygen during processing or the result of uncharacterized surface effects.

The effect of bromine on the condensed phase was examined by TGA using DuPont's Dacron[®] 900F containing tetrabromobisphenol-A. The thermograms obtained at a heating rate of $20^{\circ}\text{C min}^{-1}$ in both nitrogen and 20% oxygen in nitrogen show what appears to be two processes taking place. Oxygen appeared to have its most pronounced effect at lower temperatures.

The correlation analysis of both first and second-order decomposition showed that an overall second-order process best approximated the experimental results and therefore the reaction rates were calculated assuming an order of two. The temperatures used were 356, 369, 387°C and these results are tabulated in Table XXXI. It is obvious from these data that bromine is affecting the condensed phase decomposition of PET. The effect, however, is to increase the rate at 356°C by 50% and to increase the rate at 387°C by about 250%. Although there seems to be condensed phase retardation of the oxidative processes causing weight loss, the overall decomposition rate is higher than that of the untreated PET. It must be emphasized, however, that it is the rate constants that are being compared and not the rates of the decomposition reactions. Since these rate constants were observed to reflect the overall thermal stability of the samples their comparison is well justified. A possible mechanism for the catalytic effect of bromine on PET is shown in equation {5}

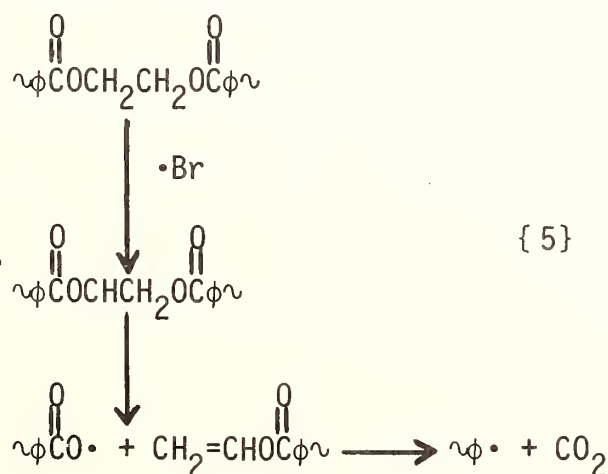


TABLE XXXI
RATE CONSTANTS FOR THE DECOMPOSITION OF DACRON[®] 900F AND THE COMPARISON TO DACRON[®] 54

% O ₂	356° C			369° C			387° C		
	k min ⁻¹ mg ⁻¹	Std. Dev. ^a	$\frac{k_{900F}}{k_{PET}}$	k min ⁻¹ mg ⁻¹	Std. Dev. ^a	$\frac{k_{900F}}{k_{PET}}$	k min ⁻¹ mg ⁻¹	Std. Dev. ^a	$\frac{k_{900F}}{k_{PET}}$
0	2.18 x 10 ⁻²	0.04 x 10 ⁻²	3.8	2.48 x 10 ⁻²	0.14 x 10 ⁻²	2.0	3.83 x 10 ⁻²	0.09 x 10 ⁻²	1.3
5	2.26 x 10 ⁻²	0.02 x 10 ⁻²	2.9	3.74 x 10 ⁻²	0.17 x 10 ⁻²	2.5	4.90 x 10 ⁻²	0.19 x 10 ⁻²	1.3
12	2.77 x 10 ⁻²	0.07 x 10 ⁻²	3.5	4.14 x 10 ⁻²	0.16 x 10 ⁻²	22.4	6.11 x 10 ⁻²	0.15 x 10 ⁻²	1.3
20	3.44 x 10 ⁻²	0.02 x 10 ⁻²	2.7	4.98 x 10 ⁻²	0.19 x 10 ⁻²	2.0	9.60 x 10 ⁻²	0.19 x 10 ⁻²	1.8

^aStandard deviation of the mean k of at least three samples.

The ratios of the rate constants for PET decomposition to those for Dacron[®] 900F show that the effect of bromine in the condensed phase is limited mostly to the low temperatures in the presence of oxygen. This effect appears to diminish as the temperature increases, again suggesting that at higher temperatures pyrolysis begins to become more significant. An alternate possibility is that the bromine in the Dacron[®] 900F was volatilized early in the decomposition at the higher temperatures so that the observed decomposition was essentially that of the PET alone.

One phosphorus-containing flame retardant was also studied. Hexaphenoxycyclotriphosphazene was added at a level of 10% of the melt before spinning. TGA analysis showed that the presence of oxygen lowers the decomposition temperature of this fiber, but not as significantly as in the case of Dacron[®] 900F samples. The differential TGA indicated that two processes are responsible for the weight loss in both the presence and absence of oxygen. The effect of oxygen, as illustrated by the differential curves, is primarily on the second process which occurs at the higher temperature. This is in contrast to the Dacron[®] 900F where the effect of oxygen was found to be on the lower temperature processes. A study of the hexaphenoxycyclotriphosphazene itself by TGA showed very little effect from the presence of oxygen; but when the differential curves were examined it became clear that the presence of oxygen either caused an additional process to occur or the rate of certain pyrolytic reactions to diminish. This suggests that a chemical reaction may take place between the hexaphenoxycyclotriphosphazene and PET in the condensed phase.

Statistical analysis of the data indicated that a second order expression gave the best description of the rate of the decomposition. Thus the rate constants given in Table XXXII, were calculated on this basis. In contrast to the Dacron[®] 900F system, the phosphorus-containing samples showed a detectable decrease in the rate at 356°C as the oxygen to nitrogen ratios increased. At 369°C the rate constants for all the oxygen to nitrogen ratios were essentially the same. As the temperature of decomposition increased to 387°C the rate in oxygen

TABLE XXXII

DECOMPOSITION RATE CONSTANTS FOR PHOSPHAZENE-CONTAINING PET (PFR) AND THE COMPARISON TO DACRON ⁵⁴

% O ₂	356 ⁰ C			369 ⁰ C			387 ⁰ C		
	k min ⁻¹ mg ⁻¹	Std. Dev. ^a	$\frac{k_{PFR}}{k_{PET}}$	k min ⁻¹ mg ⁻¹	Std. Dev. ^a	$\frac{k_{PFR}}{k_{PET}}$	k min ⁻¹ mg ⁻¹	Std. Dev. ^a	$\frac{k_{PFR}}{k_{PET}}$
0	5.12 x 10 ⁻²	0.08 x 10 ⁻²	8.6	1.03 x 10 ⁻¹	0.06 x 10 ⁻¹	8.2	1.19 x 10 ⁻¹	0.03 x 10 ⁻¹	4.2
5	4.59 x 10 ⁻²	0.03 x 10 ⁻²	5.9	1.01 x 10 ⁻¹	0.03 x 10 ⁻¹	6.7	1.24 x 10 ⁻¹	0.05 x 10 ⁻¹	3.3
12	4.55 x 10 ⁻²	0.03 x 10 ⁻²	5.7	0.99 x 10 ⁻¹	0.03 x 10 ⁻¹	5.7	1.30 x 10 ⁻¹	0.11 x 10 ⁻²	2.7
20	3.73 x 10 ⁻²	0.05 x 10 ⁻²	2.9	1.05 x 10 ⁻¹	0.04 x 10 ⁻¹	4.3	1.49 x 10 ⁻¹	0.05 x 10 ⁻²	2.8

^aStandard deviation of the mean k of at least three samples.

began to increase relative to the rate constants in 100% nitrogen. This can be misleading, however, because inspection of the ratios of the rate constants for the phosphorus-containing fiber to that of the Dacron[®] 54 indicates that the overall rate is increased on incorporation of the hexaphenoxycyclotriphosphazene. This means that although the flame retardant is affecting the decomposition processes in the condensed phase, it is not efficient enough to be effective in slowing the decomposition rate to a level below that of untreated PET. The decrease in the rate as O₂ content increases at lower temperatures may result from radical trapping by the hexaphenoxycyclotriphosphazene which becomes less significant at higher temperatures due to the dominance of pyrolysis reactions. The possibility also exists, however, that the flame retardant will volatilize at a faster rate at higher temperatures causing a decrease in the condensed phase efficiency.

Since oxidation involves a free radical mechanism, an increase in the rate of decomposition due to oxidation should be accompanied by an increase in the radical concentrations. To confirm this, electron spin resonance (ESR) was used to monitor the relative concentration of radicals in the residues. The temperatures chosen for isothermal decomposition were 356°C and 387°C with oxygen/nitrogen ratios of zero to twenty percent. The radical concentrations of all the residues were measured at room temperature with the same modulation, frequency, and microwave power. Sample weight was kept close to 10 mg to minimize any dependence of the ESR signal on sample size. The observed signal consisted of a broad singlet; thus to establish a meaningful measure of the relative number of radicals the peak to peak height was divided by the residue weight.

Figure 45 shows a plot of percent weight loss versus the normalized signal at 356°C for Dacron[®] 54. The concentration of radicals when the sample was degraded in 20% oxygen increased rapidly at a fifty percent weight loss; whereas decomposition in 100% nitrogen resulted in a significantly slower growth in radical concentration. At 387°C, as shown in Figure 46 an increase in the concentration of

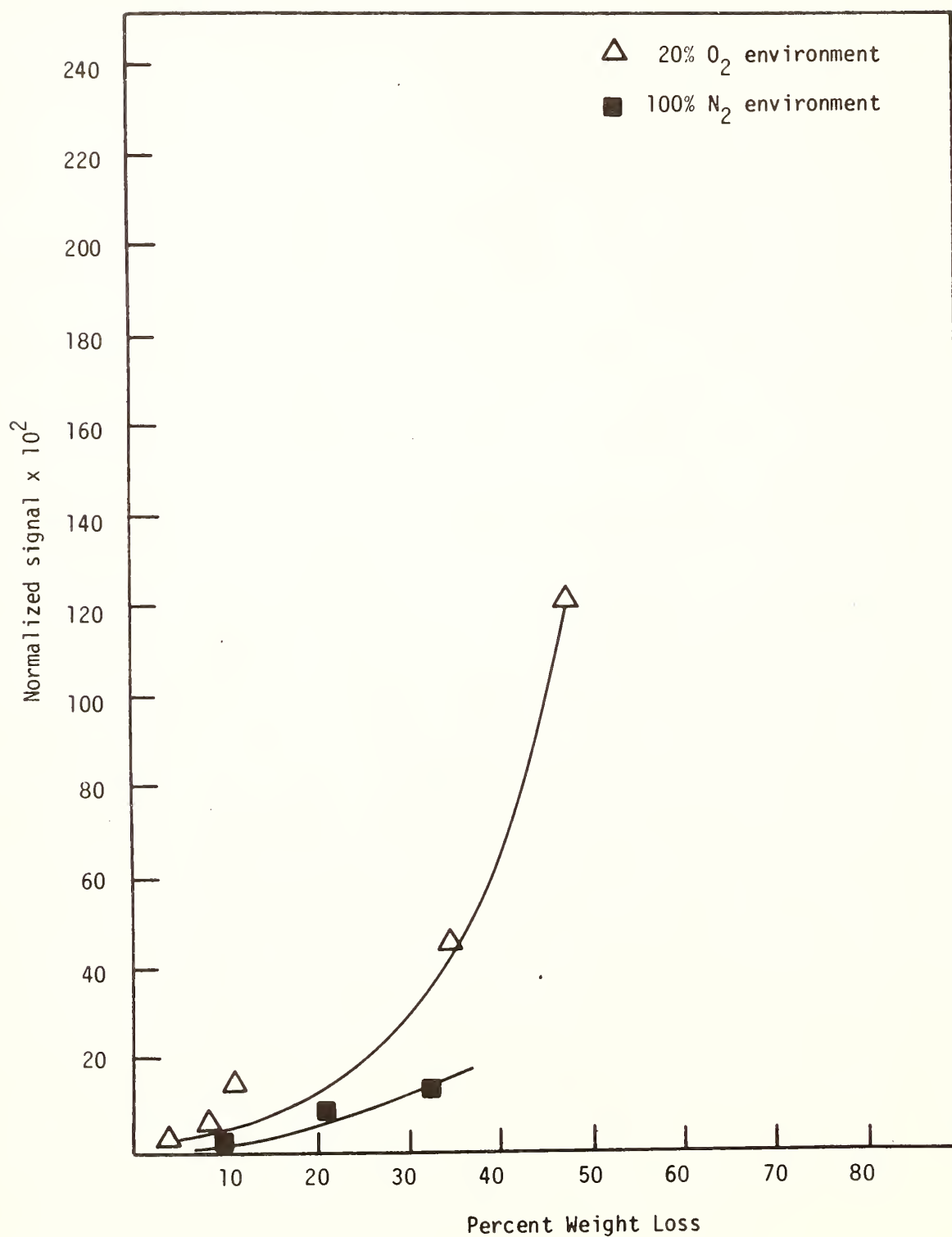


FIGURE 45. Normalized ESR signal versus percent weight loss for Dacron[®] 54 at a decomposition temperature of 356°C.

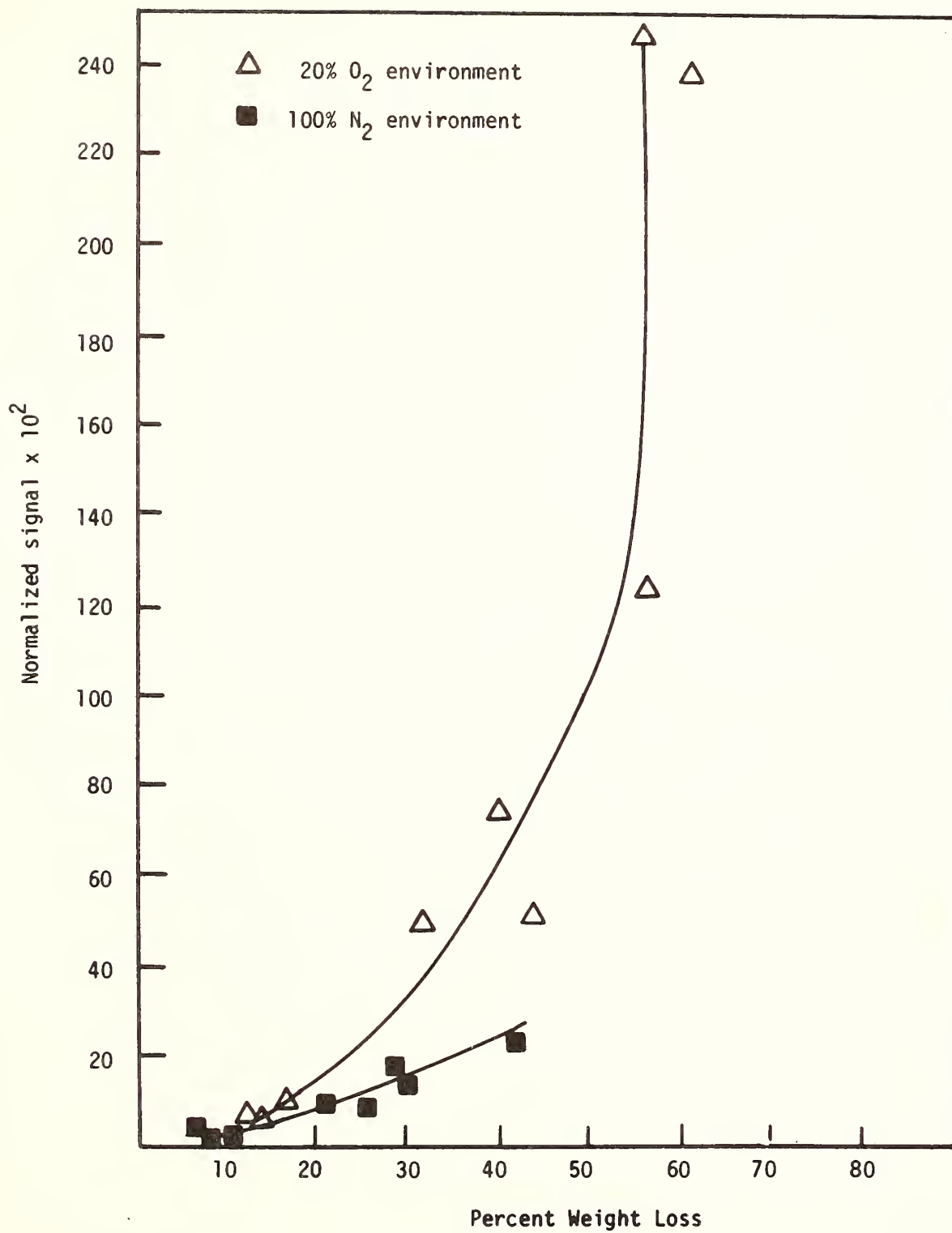


FIGURE 46. Normalized ESR signal versus percent weight loss for Dacron[®] 54 decomposed at 387°C.

radicals appeared at a 50% weight loss in both atmospheres with the rate of increase being much slower in 100% nitrogen. In comparison, the onset of radical formation in oxygen occurred earlier in the lower temperature experiments but there was little change in the curves for decomposition in nitrogen. This suggests that oxidation is more significant at the lower temperatures. This latter observation is in agreement with the earlier kinetic results obtained by thermogravimetric analysis.

The same experimental results were used to obtain an approximation of the rate of formation of radical species assuming a pseudo first-order decomposition. At 356°C the rate constants in 100% nitrogen and 20% oxygen were found to be $1.28 \times 10^2 \text{ min}^{-1}$ and $7.21 \times 10^2 \text{ min}^{-1}$, respectively. The production of radicals in 20% oxygen was over five times that found in 100% nitrogen atmospheres suggesting that oxidative degradation is significant. At 387°C the rate constants were $1.03 \times 10^3 \text{ min}^{-1}$ in 100% nitrogen and $4.56 \times 10^3 \text{ min}^{-1}$ in 20% oxygen. This represents a four-fold increase in rate.

ESR measurements for Dacron[®] 900F were made in the same manner as for the Dacron[®] 54 samples. Figure 47 shows that at 356°C radical formation commenced near a weight loss of thirty percent in both 100% nitrogen and 20% oxygen environments. The rate of radical formation, assuming a pseudo first-order reaction, was found to be $3.07 \times 10^3 \text{ min}^{-1}$ for 100% nitrogen and $5.73 \times 10^3 \text{ min}^{-1}$ for 20% oxygen.

Since not all mechanisms will lead to radical species, it should not be considered inconsistent that the order established by ESR is first order while TGA studies showed the decomposition to be approximated by second order kinetics. Based on these rate constants the formation of radicals in 20% oxygen occurred 1.9 times faster than in 100% nitrogen. The total number of radicals increased significantly when the decomposition temperature was raised to 387°C. Figure 48 shows that the increase in radical species occurred near 20% weight loss in 20% oxygen and near 45% weight loss in 100% nitrogen. When 60% of the weight was lost radical formation increased significantly for both cases. The rate constants at this temperature were found

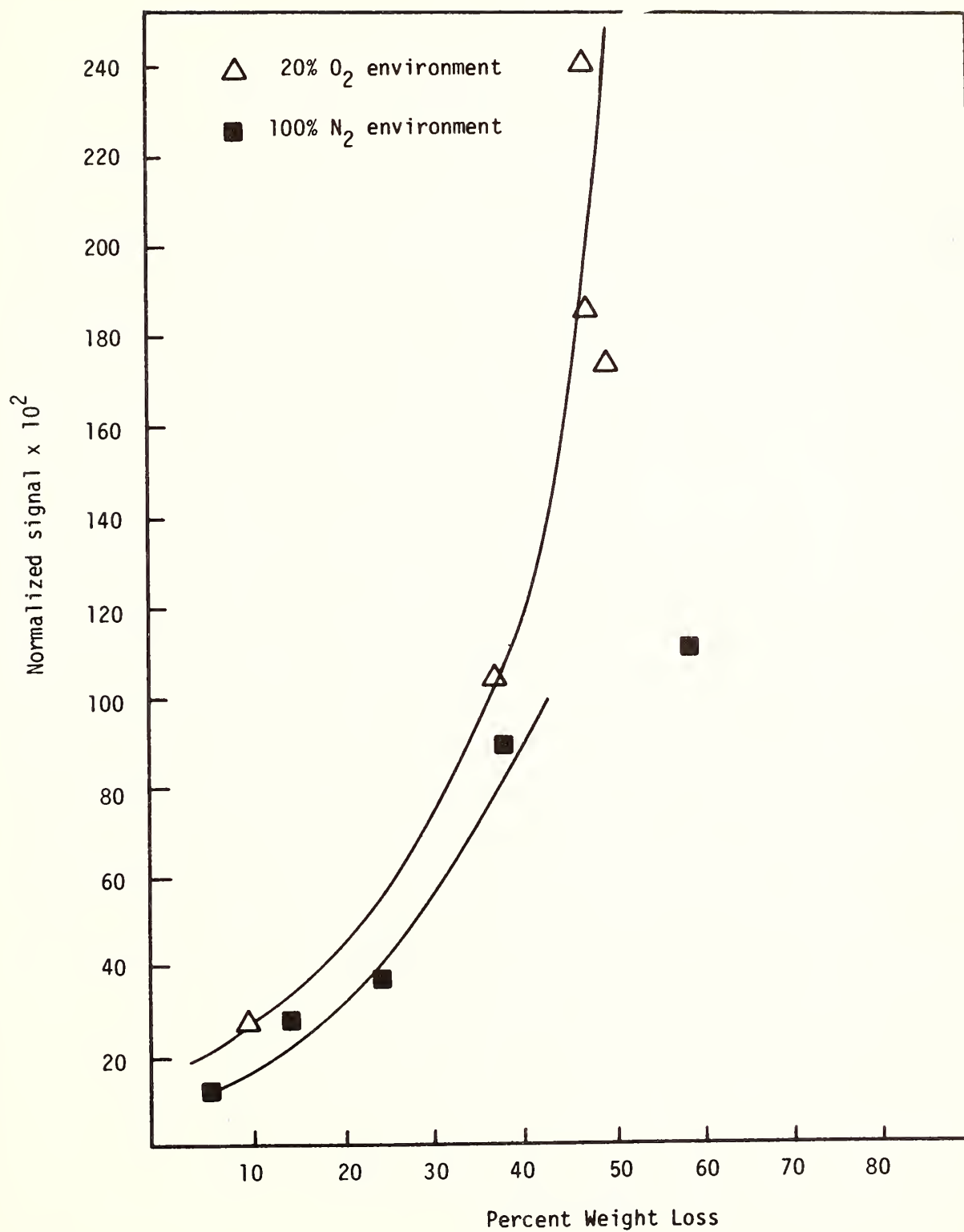


FIGURE 47. Normalized ESR signal versus percent weight loss for Dacron[®] 900F decomposed at 356°C.

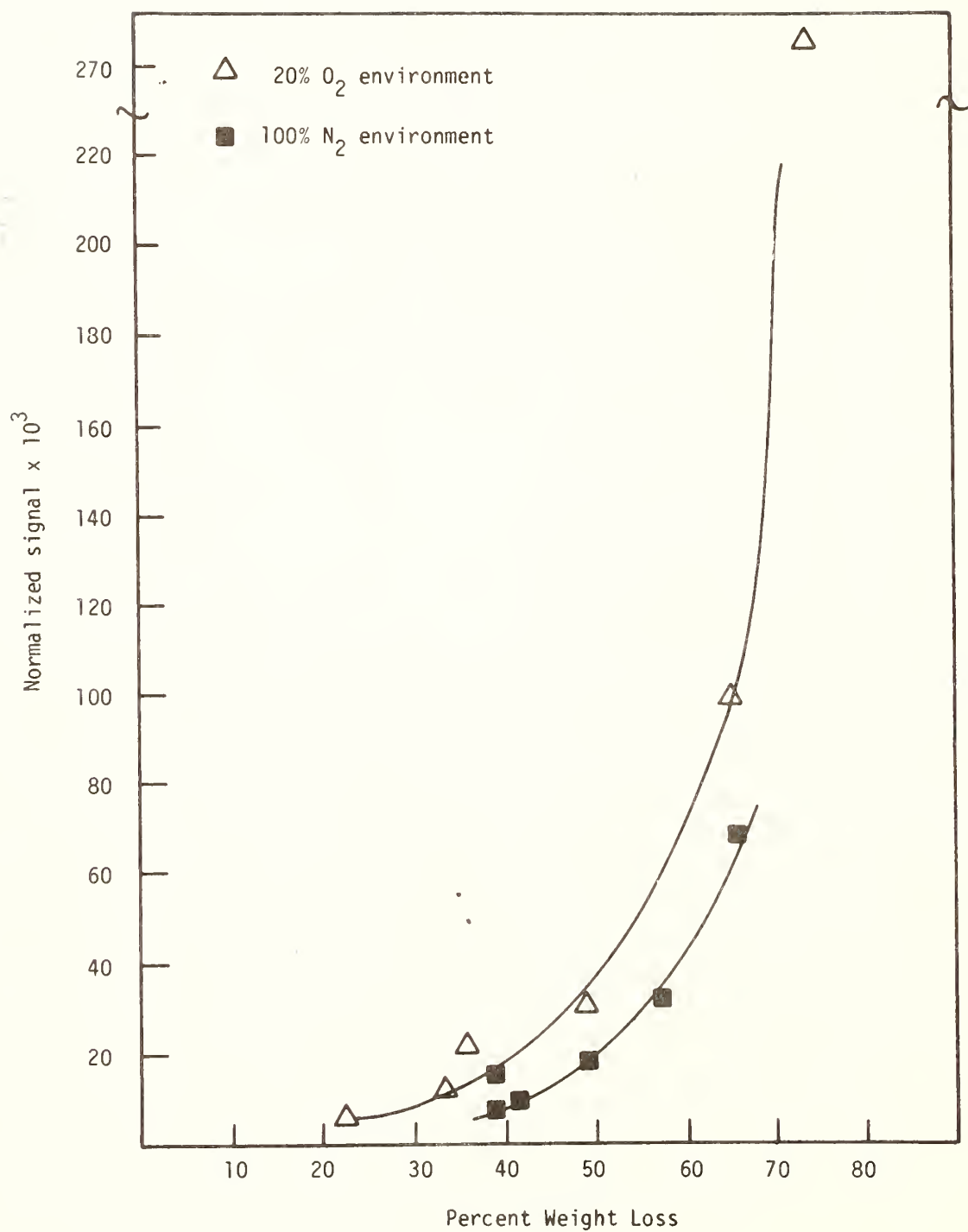


FIGURE 48. Normalized ESR signal versus percent weight loss for Dacron[®] 900F decomposed at 387°.

to be $2.33 \times 10^4 \text{ min}^{-1}$ in 20% oxygen and $7.4 \times 10^3 \text{ min}^{-1}$ in 100% nitrogen, representing a rate in oxygen which is three times faster than that in nitrogen.

The ESR measurements of the phosphazene-containing fiber residues at 356°C are illustrated in Figure 49. The rise in the number of radical species occurred at 25% weight loss in nitrogen and 35% weight loss in 20% oxygen indicating that the addition of hexaphenoxycyclo-triphosphazene inhibited the production of radicals in the presence of oxygen. The rate constants, assuming pseudo first-order kinetics, were found to be $5.64 \times 10^2 \text{ min}^{-1}$ in nitrogen and $2.54 \times 10^2 \text{ min}^{-1}$ in 20% oxygen. At a temperature of 387°C the concentration of radicals began to increase rapidly at 55% weight loss in nitrogen and 65% weight loss in a 20% oxygen atmosphere (Figure 50). This is consistent with the results at the lower temperature in that the hexaphenoxycyclo-triphosphazene retarded the onset of radical formation. The rate constants were $1.03 \times 10^5 \text{ min}^{-1}$ and $1.33 \times 10^5 \text{ min}^{-1}$ for nitrogen and 20% oxygen environments, respectively.

Although there is a high degree of scatter, the ESR data are consistent and offer supporting evidence of the results found in the TGA studies. The rate constants established by ESR and by thermogravimetric analysis are compared in Table XXXIII.

Although these data point to the existence of condensed phase interactions between PET and the phosphorus and bromine compounds, it is difficult to elaborate on the actual mechanisms of the reactions. A chain transfer mechanisms would involve the donation of a hydrogen atom to terminate a chain branching reaction and form a stabilized free radical. This would result in a constant or decreasing concentration of radical species depending on the rate of recombination reactions; or, if the free radical produced were extremely stable, it is possible that there could be an increase in radicals as oxidation and termination continue in the form of the production of stabilized radicals.

At both 356°C and 387°C the concentration of radical species formed in Dacron ^(R)900F were higher than in Dacron ^(R)54 in both

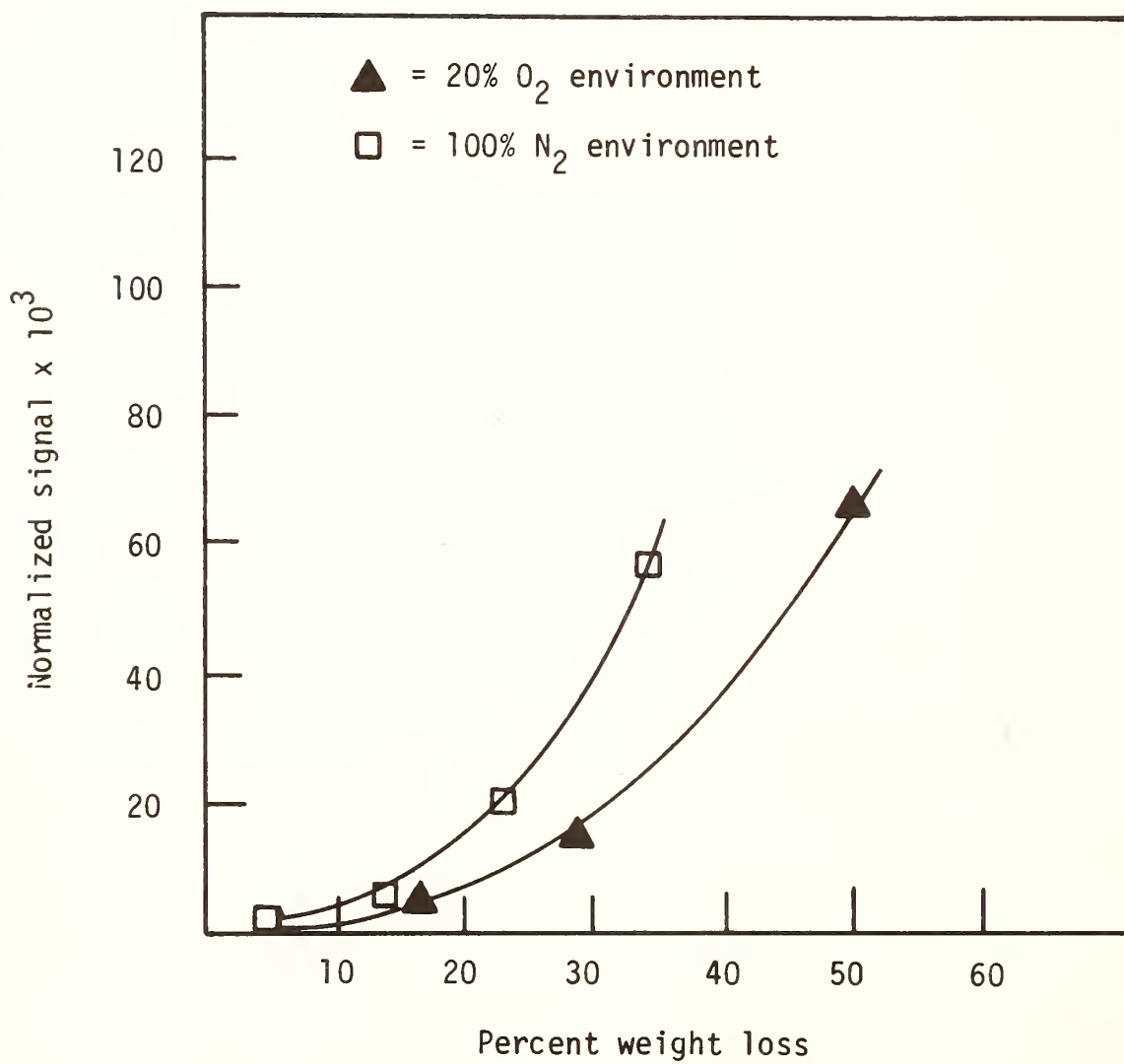


FIGURE 49. Normalized ESR signal versus percent weight loss for phosphazene containing PET (PFR) decomposed at 356°C.

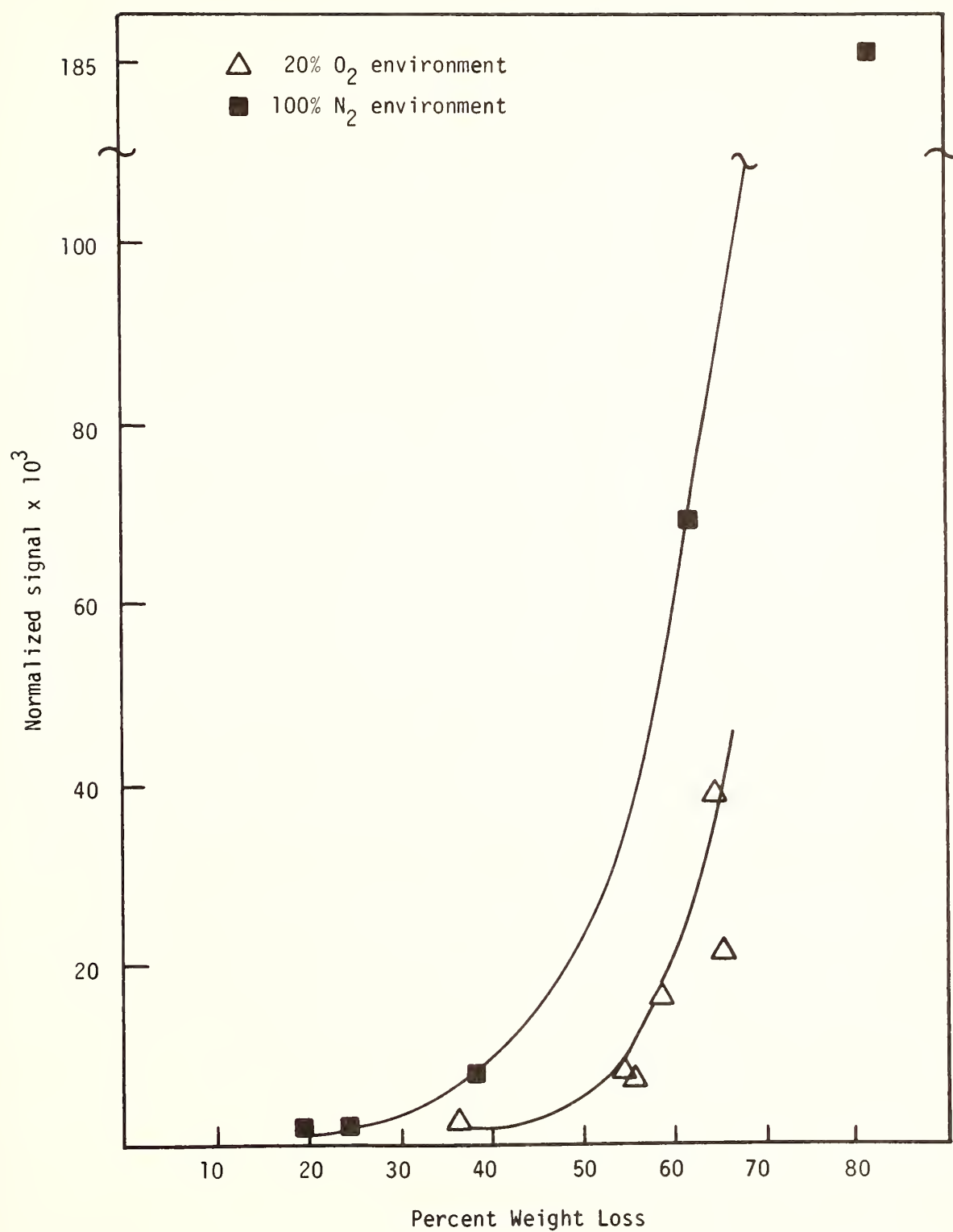


FIGURE 50. Normalized ESR signal versus percent weight loss for phosphazene containing PET (PFR) decomposed at 387°C.

TABLE XXXIII
COMPARISON OF TGA AND ESR DATA FOR PET DECOMPOSITION

% O ₂	Temperature (°C)	Dacron 54		Dacron 900F		Enka PFR $\frac{1}{10}$	
		k _{TGA} min ⁻¹	k _{ESR} min ⁻¹	k _{TGA} min ⁻¹	k _{ESR} min ⁻¹	k _{TGA} min ⁻¹	k _{ESR} min ⁻¹
0	356	5.94 x 10 ⁻³	1.28 x 10 ²	2.18 x 10 ⁻²	3.07 x 10 ³	5.12 x 10 ⁻²	5.64 x 10 ²
20		1.26 x 10 ⁻²	7.21 x 10 ²	2.77 x 10 ⁻²	5.73 x 10 ³	3.73 x 10 ⁻²	2.55 x 10 ²
0	387	2.86 x 10 ⁻²	1.03 x 10 ³	3.83 x 10 ⁻²	7.40 x 10 ³	1.19 x 10 ⁻¹	2.07 x 10 ⁴
20		5.26 x 10 ⁻²	4.56 x 10 ³	9.60 x 10 ⁻²	2.33 x 10 ⁴	1.49 x 10 ⁻¹	4.47 x 10 ³

nitrogen and 20% oxygen. The formation of radicals from the bromine-containing fiber in nitrogen was closer in Number and rate to the formation of radicals in 20% oxygen than observed with the Dacron[®] 54. This suggested that the reaction of PET with bromine represented a lower energy pathway for decomposition than the reaction with oxygen. At lower temperatures there would be a competition between oxygen and bromine, resulting in the smaller difference in the ESR curves from Dacron[®] 900F in nitrogen and oxygen. At higher temperatures, where more energy is available, and with the additional oxidative pathway, there would be a net increase in the number of radical species in the presence of oxygen.

The degree of formation of radicals in PET at 356°C and 20% oxygen is similar to the phosphorus-containing samples at the same temperature but in 100% nitrogen. This suggests that the hexaphenoxycyclotriphosphazene is serving as an initiator in the absence of oxygen to decompose the PET in the same way as the bromine appears to do in the Dacron[®] 900F. In the presence of oxygen, however, the additive serves as an antioxidant since the rate and concentration of radicals decrease, indicating an interaction between oxygen and the hexaphenoxycyclotriphosphazene. Further decomposition of the flame retardant would then enable it to act in a manner similar to that proposed by Hastie (41).

At 387°C a similar effect was observed and the phosphorus flame retardant delayed the oxidative production of radicals until 60% of the initial weight was lost, after which the concentration of radical species increased rapidly due to the volatilization of the retardant.

Using a simple heat balance scheme, and assuming a heat of combustion for PET of 6,000 cal/gram, it can be shown that condensed phase oxidation represents a significant part of the heat experienced by the condensed phase. If 80% of a one gram sample undergo pyrolytic degradation in the condensed phase, the volatile products which undergo complete combustion to carbon dioxide and water will give off 4,800 cal/gram in the vapor phase. If the remaining 20% is half oxidized in the condensed phase and then completely oxidized in the

vapor phase, 600 calories will be produced in the condensed phase and 600 calories will be added to the vapor phase. The net result is 5,400 calories being produced in the vapor phase and 600 calories being produced in the condensed phase. Since calculations by Kanury (62) suggest that a minimum of 2% and a maximum of 20% of the heat is transferred to the surface in the case of polypropylene rods, an average of 10% of the heat transferred to the surface from the vapor phase would result in a contribution of 540 calories compared to the 600 calories produced by oxidation. These values will, of course, vary depending upon the configuration of the burning sample, but they do show that the oxidative degradation that takes place in the condensed phase can be significant, even if the contribution to the overall scheme is small.

2. Flame Retardant Polyester

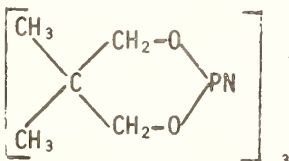
2.a. Inherently Flame Retardant Polyester:

The development of an inherently flame retardant polyester has been undertaken as a proprietary project of the American Enka Company under the direction of Dr. Gerald W. McNeely. Although a portion of this work was carried out in cooperation with the ETIP consortium, all of the actual development work was conducted by American Enka at their own expense; thus the fiber is a proprietary product of American Enka.

A variety of aryloxycyclotriphosphazenes were synthesized and screened as potential flame retardant additives for PET. Phosphonitrilic chloride undergoes nucleophilic substitution reactions with nucleophiles such as alkoxides, thiolates, primary and secondary amines, and ammonia. Thus a very large number of derivatives are possible. Unfortunately none of the alkoxo derivatives examined, with the exception of the fluorinated derivatives, were found to have sufficient thermal stability to be incorporated into PET. This also was the case with the various amine and ammonia derivatives evaluated. As a result all further work was devoted to the aryloxycyclotriphosphazenes. These were synthesized by the reaction of $(\text{PNCl}_2)_3$ with sodium phenoxide in a fairly high boiling solvent such as dioxane or toluene to give the best yield of completely substituted product. In Table XXXIV lists a number of compounds of this type along with some physical properties.

Although a large number of phosphazenes were evaluated, only hexaphenoxycyclotriphosphazene (PFR-1) has been extensively studied. Most of the other phosphazenes were ruled out as potential flame retardant candidates after a limited laboratory evaluation. Generally this evaluation consisted of first checking the thermal stability of the flame retardant and eliminating most of the compounds that decomposed below 280°C . Compounds with thermal stability greater than 280°C were mixed with PET, then the resultant polymers were either spun into yarns or pressed into films. The oxygen index values of

TABLE XXXIV
CYCLOPHOSPHAZENE PHYSICAL PROPERTIES

Compounds	M.P., °C	TGA owl*, °C	P, %
$\{(C_6H_5O)_2PN\}_3$	116	290	13.4
$\{(C_6H_5O)_2PN\}_4$	86	314	13.4
$\{(p\text{-Br}C_6H_4O)_2PN\}_3$	174	350	8.0
$\{(C_6H_5)_2PN\}_3$	153	275	11.8
$\{(p\text{-CH}_3C_6H_4O)_2PN\}_3$	120	310	12.0
$\{(p\text{-NO}_2C_6H_4O)_2PN\}_3$	269	320	9.6
$\{(C_6H_5\text{-}C_6H_4O)_2PN\}_3$	277	280	8.1
$\{(C_6H_5CH_2O)_2PN\}_3$	49	225	11.95
$\{(ClC_6H_4O)_2PN\}_3$	155	310	10.3
	340	275	21.0

* onset of weight loss, N_2 , $10^0/\text{min}$.

the yarns and films were determined and used as the initial measurement of flame retardancy. Based on OI results, a few of these compounds were as effective as PFR-1 as flame retardants for polyester, but were eliminated as potential candidates because of other deficiencies such as the following:

- compound would not mix with PET;
- vapor pressure too high and compound volatilized during yarn preparation;
- compound too expensive to prepare;
- compound reacted with PET causing polymer degradation.

There are four possible times that PFR-1 can be added to the PET process: (1) before ester interchange; (2) before polymerization; (3) after polymerization; (4) during melt spinning. The purity of PFR-1 has a direct bearing on when it can be added to the process. In the laboratory, very pure PFR-1 (M.P. 112-114°C) has been added to the ester interchange reactants and retained through the entire process. However, experience with pilot plant quantities of PFR-1 has indicated that it will contain residual chloride which may cause polymer degradation, depending upon the level present. In order to decrease the effect of chloride upon polymer properties, a minimum contact time between molten polymer and PFR-1 is suggested. Injection of the flame retardant into the molten polymer, followed by mixing, is the preferred method, especially if the flame retardant contains more than 1% chloride. Although less than 1% chloride in the additive is preferred, it is not mandatory. The addition of 10 wt. % of impure PFR-1 to polyester via the pin mixer did not have a detrimental effect on the physical properties of the yarn. It was possible to obtain a yarn with 4 gpd, and elongation of 30%, and a Gardner b value of 4.2. The heat and light stability of the yarn was comparable to that of normal PET yarn.

The flame retardant properties of polyester containing phosphazenes were determined by OI and the children's sleepwear test (FF 3-71). The OI measurements were carried out on knit tubes and films. In order to prevent the molten polymer from dripping or melting away from the

flame front during burning, glass fibers were incorporated into the knit tubes and films. The relationship between OI and wt. % PFR-1 for both knit tubes and films are given in Figure 51

These results indicate that the effect of PFR-1 begins to level off between 13 and 15%. The OI of PET containing 10 wt. % PFR-1 is 0.255 compared to a value of 0.243 for Dacron[®] 900F.

Although OI measurements are not directly related to any flammability standards, the recent suggestion of van Krevelen (63) of a linear relationship between OI and char residue of polymers has increased the utility of OI measurements. One of the major ways to decrease the flammability of polymers is to enhance the char residue formation. The relationship between OI and char residue of PET samples containing different amounts of PFR-1 are shown in Figure 52

When 100% PET fabrics are tested in the children's sleepwear test the burning polymer drops away from the sample. If PET fails the sleepwear test, it usually does so by the melt drip burning in the bottom of the cabinet. Polyester samples containing at least 8 wt. % PFR-1 have not failed FF 3-71 in the unseamed state, however, fabrics seamed with untreated cotton thread and ignited at the seam fail the test.

From these results it can be concluded that the flame retardancy of PET yarns and fibers can be improved by the addition of PFR-1 to the polymer. This material does not adversely affect the physical properties of PET, in fact, the addition of PFR-1 can improve the heat and light stability of PET as well as improving its dyeability with disperse dyes. When PET yarns or fibers containing PFR-1 is blended with other fibers such as modacrylics or rayon, the resultant blends also have improved flame retardancy compared to similar blends containing normal PET. Preliminary experiments also indicate that polyester/cotton blends in which the polyester portion contains 10% PFR-1 can be successfully rendered flame resistant by the application of existing phosphorus-based topical finishes.

2.b. Grafting Studies:

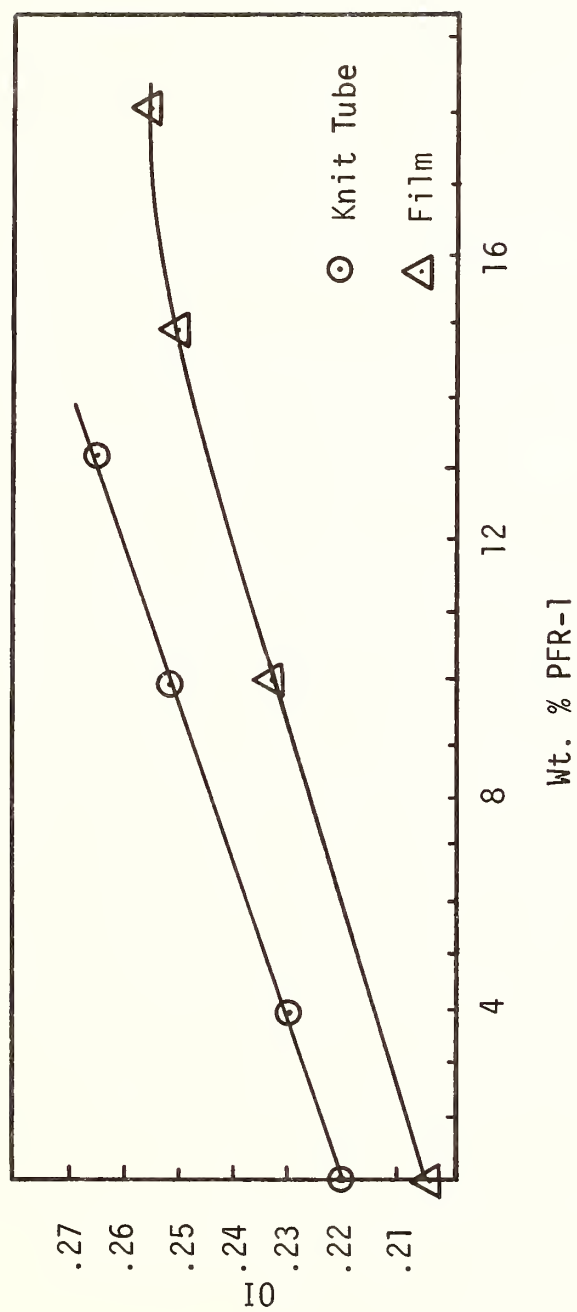


FIGURE 51. IO as a function of hexaphenoxyposphazene (PFR-1) content in PET.

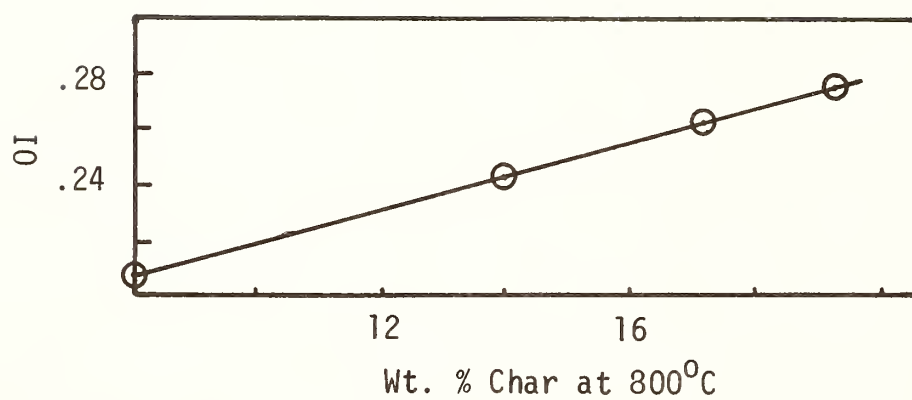


FIGURE 52. OI as a function of the residue from PET at 800°C.

A number of vinyl functional monomers containing bromine and/or phosphorus are available in laboratory or developmental quantities from standard commercial sources. Efforts were made to obtain samples of as many of these as possible for screening in the radiation fixation studies at RTI. However, there were some particular structures which were not commercially available but which would seem to offer particular promise as constituents in flame retardant formulations for blends. A program was thus initiated under the direction of Dr. James J. Duffy at Hooker Chemicals and Plastics Corporation to design and synthesis a series of special phosphorus-containing monomers for the grafting studies at RTI.

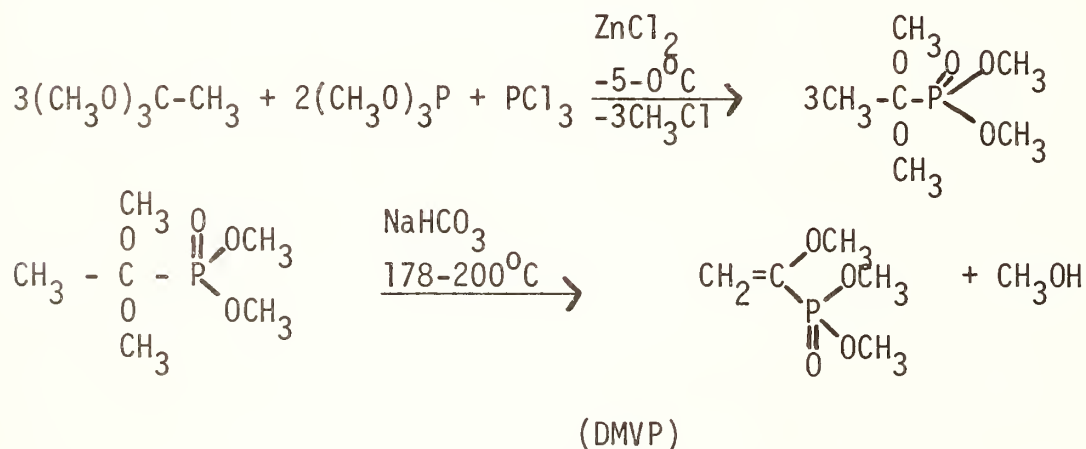
Six unsaturated phosphonates were successfully prepared. As the lowest member of the alkyl series, methyl was chosen for their ester groups so as to minimize monomer molecular weight and fuel load derived therefrom.

The most promising of these, N-(Dimethylphosphonomethyl) acrylamide (NDPA) was prepared directly from excess trimethylphosphite (TMP) and freshly recrystallized N-methylolacrylamide (NMA) using the method of Duffy, Golborn and Scharf (65). Their reported procedure was modified after some experimentation to simplify workup and reduce inhibitor content of the product. In this modified procedure, the reaction solution was stripped partially, filtered, and then further stripped leaving the product as a residue. Eliminated from the earlier procedure were the addition of benzene and hydroquinone, and subsequent filtration and stripping steps. This modified procedure was used in a successful 25 mole scale laboratory preparation which yielded 5 Kg of product.

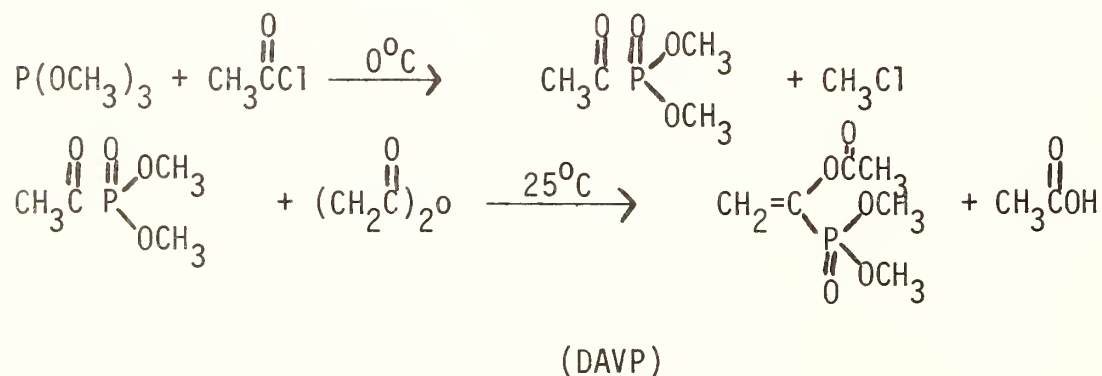
One obvious problem with this product was its unpleasant, penetrating odor derived from residual amounts of TMP. This problem was not solved by using a lower pressure (0.1 mm) at the same temperature ($\approx 60^{\circ}\text{C}$) in the final stripping step. Use of significantly higher temperatures at a plant-feasible pressure (10-20 mm) to achieve better TMP removal seemed unlikely because of the observed propensity of NDPA to polymerize. However, it was shown that the odor problem could

be overcome by adding just enough water to hydrolyze any residual TMP. To avoid hydrolysis of NDPA, it may be necessary to add some base or buffer in order to maintain neutrality.

Use of the Golborn and Dever published procedure (66, 67) resulted in a convenient laboratory preparation of dimethyl 1-methoxyvinylphosphate (DMVP) in 65% overall yield.



Dimethyl 1-(acetoxy)vinylphosphonate (DAVP) was prepared by the Golborn route (68). Its precursor, dimethyl acetylphosphonate, was conveniently prepared in 81% yield from TMP and acetyl chloride at 0°C.



Four acetylating agent and catalyst combinations were evaluated for the enolacetylation of the diemthyl acetylphosphonate. These were acetyl chloride with zinc borate and with pyridine, and acetic anhydride with triethylamine and with pyridine. The combination of acetic anhydride with pyridine proved superior on the basis of color and conversion (about 85% in 17 hours at ambient temperature).

High vacuum distillation proved unsuccessful for the isolation of

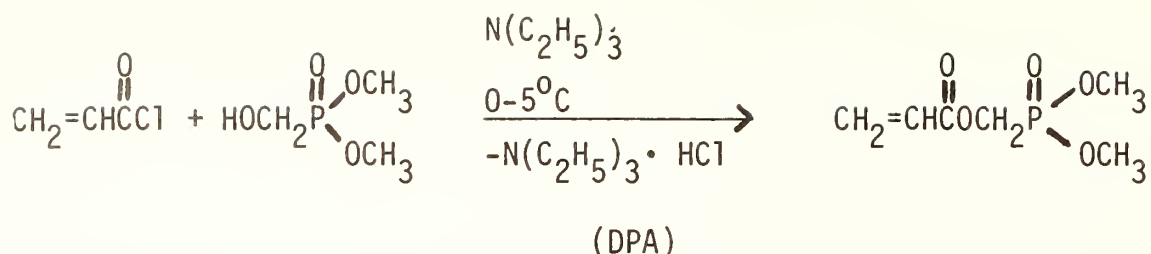
DAVP from reaction mixtures containing pyridine, acetic acid and acetic anhydride. An involved workup procedure was then used which resulted in significant loss of product due to both its alkaline hydrolysis and its water solubility. The best achieved yield of high purity material was 55%. That DAVP is a low melting solid was apparently not known to previous workers.

Dimethylphosphonomethyl acrylate (DPA) was prepared by acryloyl chloride esterification of dimethylhydroxymethyl phosphonate. The latter was conveniently synthesized in good yield and purity by a new process recently developed at Hooker.

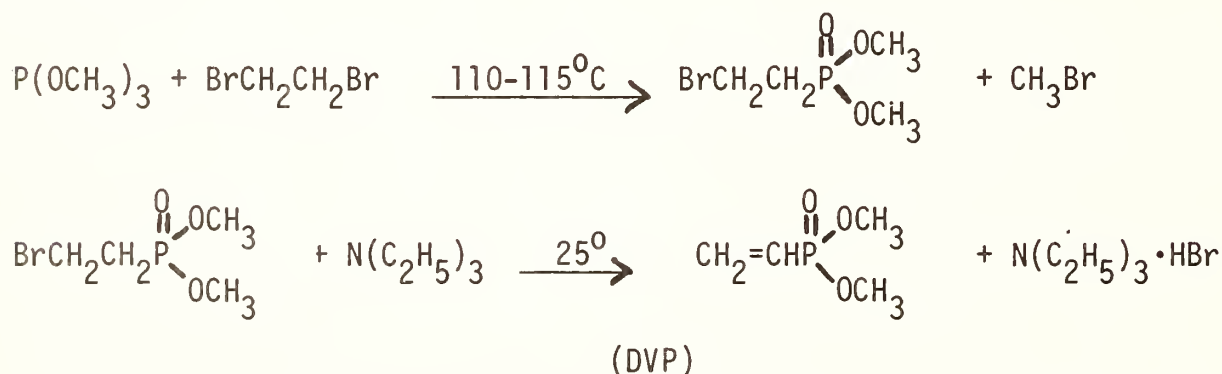
The technique for preparation of dimethylhydroxymethyl phosphonate involves cautious, dropwise addition of triethylamine to a stirred and externally cooled mixture of aqueous formaldehyde and dimethyl phosphite. No exotherm was observed until sufficient triethylamine had been added to neutralize the acid constituents. Thereafter, large quantities of free triethylamine must be avoided in order to maintain control of the exothermic reaction. This is especially true early in the reaction where dilution of reactants by product is not extensive.

The reaction is conveniently monitored by observing the disappearance of DMP using NMR. This is accomplished by observing the resonance located at $\delta=0.88$ which is one resonance of the doublet ($J=697\text{HZ}$) for the hydrogen attached to phosphorus in DMP. Triethylamine is added until this resonance is completely gone. The residue obtained on stripping under high vacuum proved distillable at 110°C under a pressure of 0.1-0.2 mm.

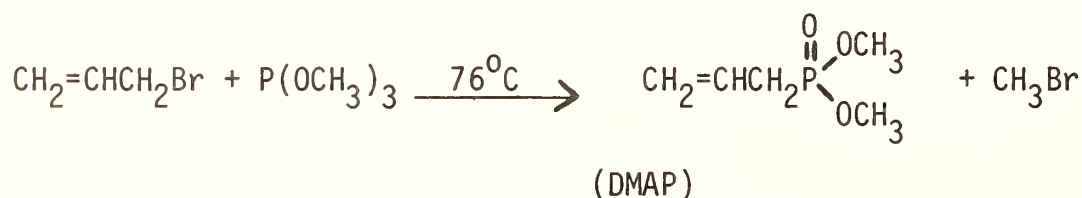
The purity of the residue was adequate for the acryloyl chloride esterification in which triethylamine was used as an acid acceptor. Significant losses of DPA, which occurred during water washings to remove triethylamine hydrochloride, resulted in a crude yield of 65%. Distillation using hydroquinone inhibitor gave a 53% overall yield of DPA based on starting DMP.



Dimethyl vinylphosphonate (DVP) was prepared by the Zenftman and Colder route (69). The Arbusov reaction of TMP with excess 1,2-dibromethane resulted in poor yields (15-30%) of the desired 2-bromomethylphosphonate; the major reaction product was dimethyl methylphosphonate formed by the methyl bromine catalyzed isomerization of TMP. The crude dimethyl 2-bromoethylphosphonate was dehydrobrominated with triethylamine.



Dimethyl allylphosphonate (DMAP) was prepared conveniently by the procedure of Arbusov and Razumov (70). This reaction, which involved refluxing excess allylbromide with TMP, resulted in a 48% yield of distilled DMAP.



Unsuccessful attempts were made to prepare several other monomers containing both phosphorus and bromine using proprietary technology from Hooker Chemicals and Plastics Corporation.

Attention was then turned to radiation grafting as a technique for imparting durable flame resistance to PET fabrics. The methodology for grafting flame retardants and related materials to 100% cellulosic materials has been quite well worked out in previously published

studies by several groups of workers. However, little has been done with grafting onto polyester. For this reason, initial investigations at RTI under the direction of Dr. Raimond Liepins have dealt with devising FR systems amenable to radiation fixation on PET.

The work with the pure polyester system was divided into two essentially separate phases. In the first, efforts were made to determine the effect of distribution of the flame retardant within the grafted polyester system. This was done with two model monomers, one based on phosphorus, and the other on bromine. Diethylvinylphosphonate (DEVP) was tentatively selected for the phosphorus studies while vinylbromide (VBr) was used for the bromine investigations. The initial studies were conducted on single polyester yarns (150/96 semidull) supplied in filament form by American Enka Company. The vinylbromide was supplied by Ethyl Corporation and the diethylvinylphosphonate synthesized by Hooker Chemicals and Plastics Corporation.

The grafting procedures have involved $^{60}\text{Co}_\gamma$ radiation to initiate the free radical reactions. A series of initial investigations showed no discernible differences in the percent weight gain obtained with scoured and unscoured yarns; thus all subsequent work has been carried out on unscoured samples. The samples were de-gased by means of three freeze-thaw cycles to at least 10^{-5} torr. In most cases, the grafting was performed using a mutual irradiation technique in a small glass ampule at dose rates of from 0.01 to 0.1 Mrad/hr. Following irradiation, the fiber samples were extracted with solvents for the homo or copolymers, first at room temperature and then at elevated temperature. The extracted fibers were vacuum dried to constant weight and stored in a desiccator for subsequent evaluation. Data for weight gain achieved during grafting was obtained following this drying procedure.

In general, the vinylbromide was found to graft with little difficulty. The percent weight gain increased linearly with total dose (time) without any induction period when grafting from a DMSO solution at room temperature. Preswelling of the fiber in ethylene dichloride produced a parallel dependence of weight gain on total dose, but displaced 1% higher on the weight gain axis. The addition of a small

amount of DMSO or hexamethylphosphoramide increased the rate of grafting markedly. This was followed by a gradual decrease with increasing amounts of either of the two materials. The largest increase in weight gain was realized at $\frac{1}{2}$ to 1 molar concentration of either of the two liquids. A similar rate effect has been observed in earlier experiments on the grafting of styrene onto polyester. In general, the best approach to increased weight gain seemed to be through the use of an organohalogen compound which is capable of functioning as both a swelling agent and a radiation sensitizer. The use of solubility parameter correlations in the choice of non-halogen containing swelling agents led to no improvement in weight gain in these studies. On the other hand, the use of organohalogen compounds as swelling agents increased the weight gain by more than 100%. In summary, the evaluation of the various vinylbromide grafts gave the following results:

filament diameter increased uniformly with the percent weight gain from 14.4 for the 2.9% graft to 16.9 for the 24.4% graft.

OI increased uniformly with the percent weight gain from 20.8 for the 0.5% graft to 27.9 for the 24.4% graft.

char yield the increase in char yield is not uniform with the percent weight gain, however, grafts with percent weight gains of more than 5 gave increased char yields of 1 to 6% above control.

tensile strength showed only a slight, non-uniform variation (4.4 to 4.8 g/denier) for the various grafts and in no case did grafting impair the tensile strength of the fiber.

elongation (reported as the ratio of the elongations of the sample to control $\times 100$) the most spectacular change that the grafting produced in the fibers was in imparting to the greater elasticity; the increased elasticity (elongation at the yield point more than 240%) was obtained at the lower grafting levels (up to 5.5%) which then decreased slightly to about 190% as the grafting level increased. The sole exception was the 24.4% graft, which was the most elastic fiber encountered and had an elongation of 298% and a tensile strength of 4.6 g/denier.

Grafting of VBr, as well as VBr₂, and VCl₂ led to colored grafts. It was found that this problem could be eliminated by co-grafting with other monomers, grafting in the presence of morpholine, or grafting at temperatures below -44°C.

Grafting of VBr on PET fiber that did not contain TiO₂ led to

clear grafts, however, drying of the extracted, grafted fiber in a vacuum oven at 50°C resulted in a colored graft. Thus, the absence of TiO_2 does not eliminate the discoloration of VBr grafts.

Grafting of VBr at 81°C did not seem to offer any advantages over RT or below RT grafting as the add-on was only 17.7%. Grafting of vinyl bromide at -64°C led to a colorless graft (8.2% add-on at 2.1 Mrads) which discolored only slightly when dried in a vacuum over at 50°C/16 hrs.

Since the samples in the grafting experiments were all in the form of individual yarns or fibers, it was necessary to develop a modified technique for measuring the oxygen index of these materials. After several attempts, a glass holder was developed which permitted one fiber or one yarn to be measured in a vertical position in the oxygen index tester. This material not only permitted the determination of the OI value, but also an estimation of the char yield as the material burned in the tester. A paper describing the details of this procedure, including data on PET fibers and comparison of the fiber samples, has been published. (64)

The effect of the location of flame retardant grafting on the PET yarns was then investigated. Samples were prepared using VBr and DEVP in which it was expected that the retardants would be grafted either on the surface or uniformly throughout the yarns. This was accomplished by varying the amount of ethylene dichloride preswelling to which the samples were subjected. For comparison, samples were also prepared having the ungrafted flame retardant homopolymer deposited on the surface of the yarns from solution. These samples were studied by OI and scanning electron microscopy.

The scanning electron micrographs were obtained from 1-2 μ thick cross-sections. These were obtained by embedding the fibers in a Dow Epoxy resin and cutting the sections with a Reichert ultramicrotome. A scanning electron micrograph showing the thickness of a section through the embedment is given in Figure 53. The fiber cross-sections are seen in the top of the micrograph. It may be noted that all these micrographs were obtained on sections which were

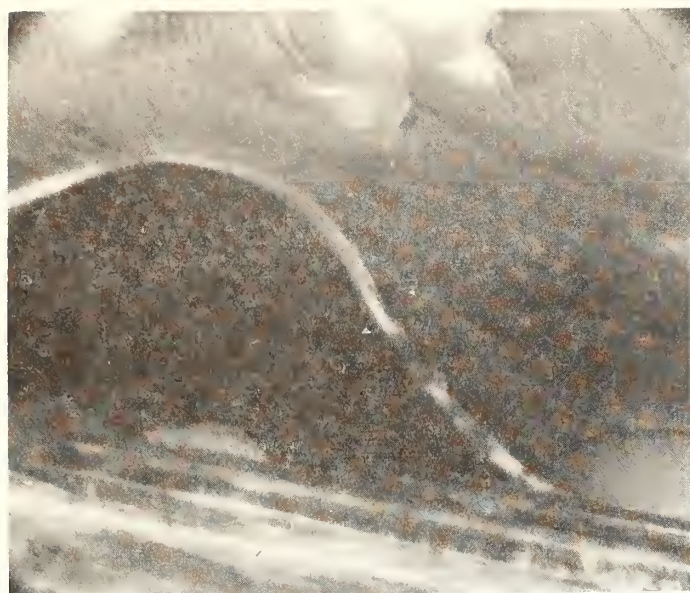
deposited on carbon stubs with no further preparation. No carbon coating was required.

In some of the sections part of some fibers would break loose from the embedding material revealing the thickness of the fiber cross-section. This is shown in Figure 54 where the fiber cross-section is shown to be 1μ thick. The plot of intensity of fluorescent X-rays versus energy of the X-rays for PVBr coated fiber is given in Figure 55. Location of the L and K emission lines for bromine are given by the vertical bars at the top of the figure. The secondary electron image of the cross-section from which this plot was obtained is given in Figure 56. The L emission line of the plot (the white part of the spectrum in Figure 55) was used for mapping, i.e. to indicate from what part of the sample the X-rays are emitted. Figure 57 shows a map indicating extremely good definition of the boundaries of the fiber seen in Figure 56. In order to ascertain that such a map actually indicated the site of bromine atoms and not especially favorable topography at the boundaries of the fiber for emissions of all X-rays, a map was obtained with a "window" corresponding to background (see white part of Figure 58 for the "window"). Such a map is presented in Figure 59 and is featureless. This procedure was routinely followed for subsequent maps.

The secondary electron image and bromine L map for the fiber to which vinyl bromide had been grafted are given in Figures 60 and 61. It can be seen that in this case the graft is localized at the surface.

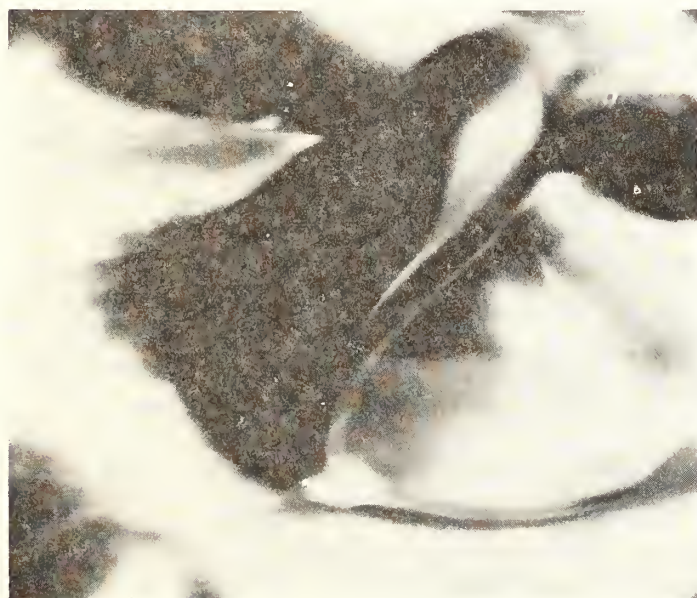
The secondary electron image, plotted as intensity versus energy of emitted X-rays and the phosphorus K_{α} plot for the fiber to which diethyl vinyl phosphonate had been grafted are given in Figures 62 and 63. The graft is shown to be distributed evenly through the cross-section of the fiber. This interpretation can be made with confidence because of the excellent resolution demonstrated in the previous maps. An enhanced version of Figure 63, in which the contribution to the map from some of the background evident in Figure 63 has been subtracted, is shown in Figure 64.

Once the location of the model flame retardant grafts had been



10 μ

FIGURE 53. SEM photomicrograph showing a cross-section of embedded PET fibers.



5 μ

FIGURE 54. PET fiber cross-section partially freed from embedded medium.

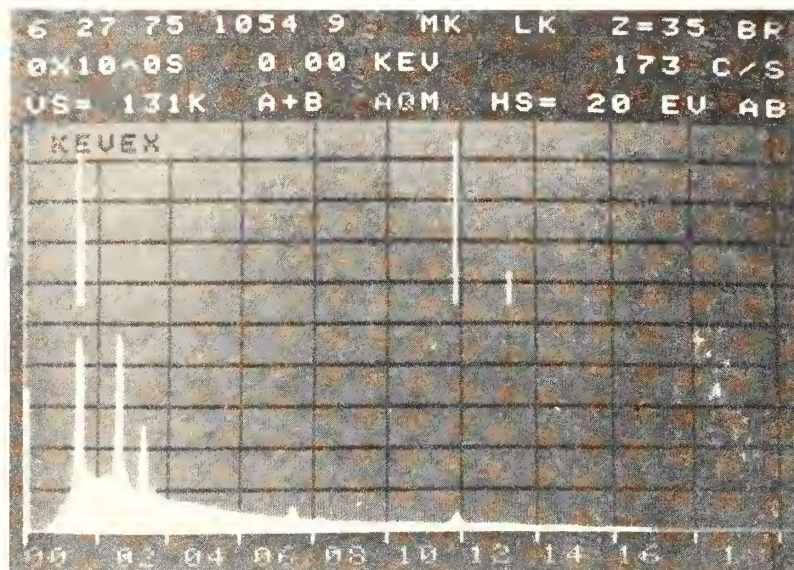
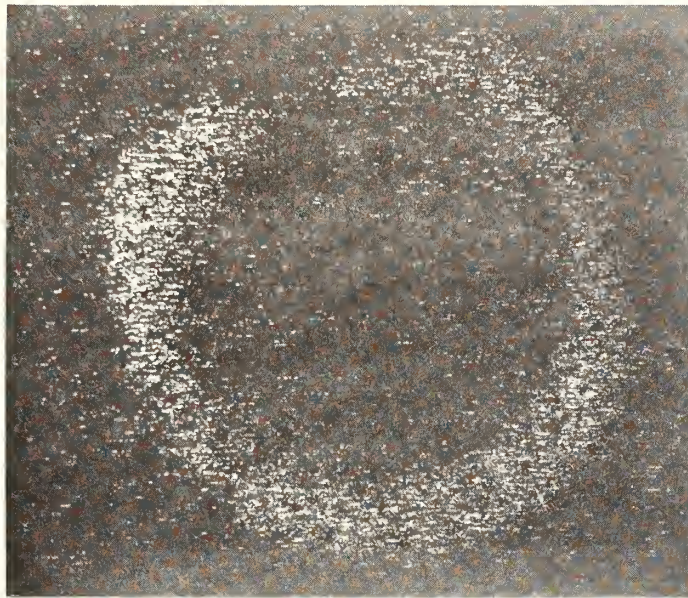


FIGURE 55. Energy spectrum for x-rays emitted from a PET sample solution coated with poly(vinyl bromide).



5 μ

FIGURE 56. Secondary electron image of sample yielding energy spectrum in figure 55.



5 μ

FIGURE 57. Bromine L x-ray map for sample shown in figure 56 using "window" indicated in figure 55 (white portion of spectrum).

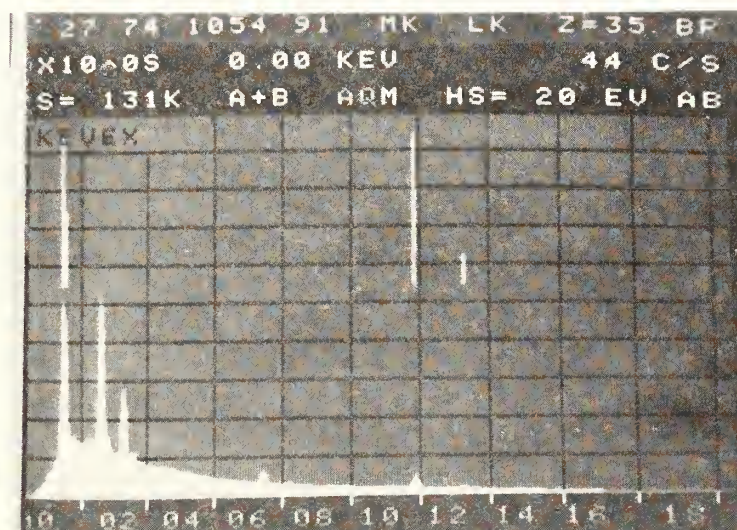
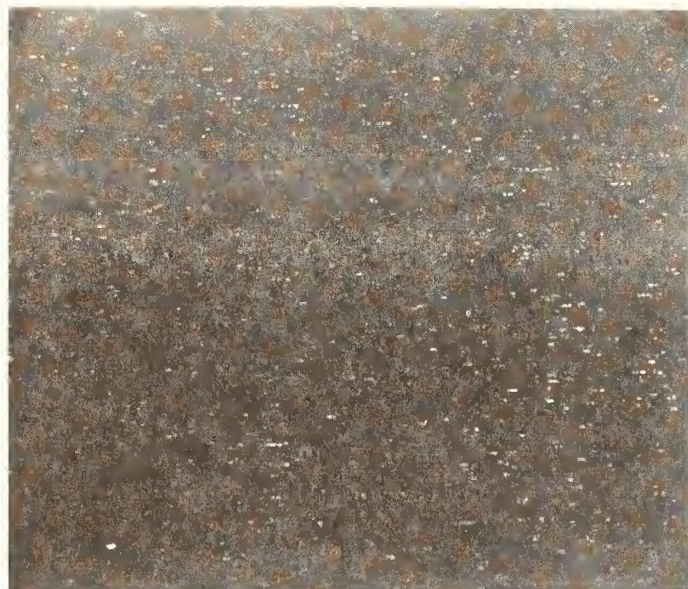
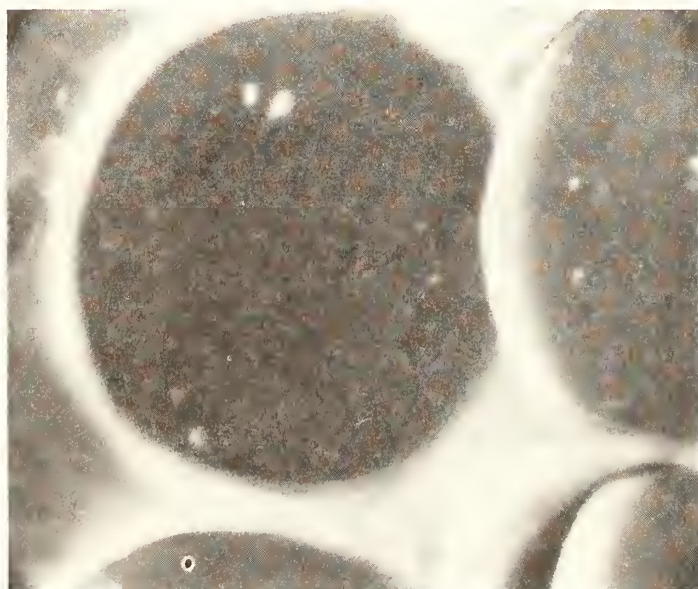


FIGURE 58. Energy spectrum from sample shown in figure 56 showing "window" on background map used for map in figure 59.



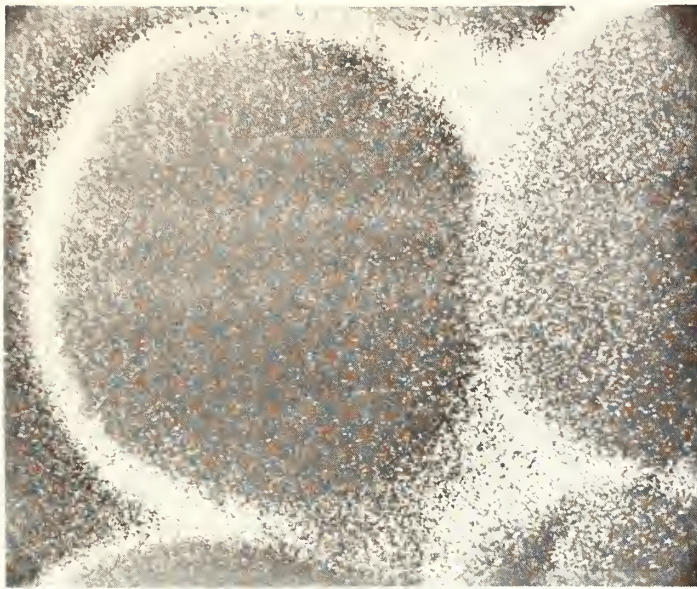
5 μ

FIGURE 59. Background x-ray map obtained from cross-section shown in figure 56 using window in figure 58.



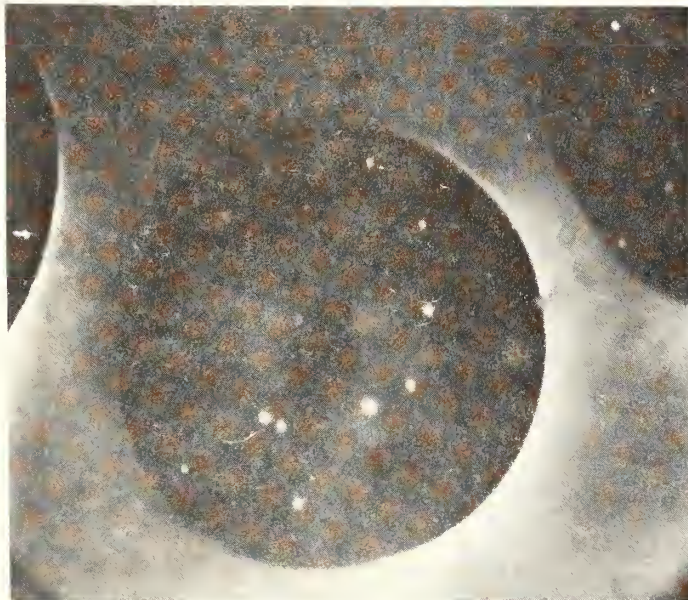
5 μ

FIGURE 60. Secondary electron image from a PET fiber to which vinyl bromide has been grafted.



5 μ

FIGURE 61. Bromine L x-ray map for fiber cross-section depicted in figure 60.



5 μ

FIGURE 62. Secondary electron image from a PET fiber to which diethyl vinyl phosphonate has been grafted.



5 μ

FIGURE 63. Phosphorus K x-ray image of the cross-section depicted in figure 62.



5 μ

FIGURE 64. Enhanced version of figure 63.

determined with certainty, it was possible to develop a correlation between the retardant location and its efficiency as measured by OI. These results are presented in Table XXXV. The placement of the PVBr in a uniform distribution throughout the fibers enhanced its flame retardant efficiency the most, followed by surface grafting and solution coating. The coating method seemed to be the least efficient in terms of raising the OI. Uniform grafting also resulted in a more efficient utilization of the poly(DEVP) as compared to surface grafting. Apparently those retardants such as PVBr and poly(DEVP) which do not possess a high degree of thermal stability become more efficient as they are incorporated deeper inside the filaments.

In order to confirm this interpretation, an attempt was made to graft vinyl bromide in such a way that it would reside predominately in the core of the filaments. This involved preswelling the fibers in ethylene dichloride and VBr followed by exposing the treated samples to ambient air before irradiation. It was hoped that in this way the VBr in the outer levels would be lost by evaporation leaving the majority of the retardant in the core.

This technique was only partially successful. Core grafting was achieved but only at a low add-on level. A core grafted sample was produced with a 1.2% add-on of grafted retardant and this sample exhibited an OI value of 21.9. In order to reach this same OI using homogeneously grafted VBr required an add-on of 2.5%. If these data can be considered as reliable indicators of flammability behavior at these low levels of treatment, this would tend to confirm the interpretation of the previous data.

In a concurrent series of experiments, various phosphorus compounds deemed to have potential as commercial flame retardants for polyester and polyester/cotton blends were evaluated in radiation grafting experiments on PET yarns. Some of the compounds studied were specifically designed and synthesized by Dr. Howard Day of Hooker Chemicals and Plastics Corporation. Other were obtained from a variety of commercial suppliers. The monomers evaluated are tabulated in Table XXXVI. In several cases copolymerization and

TABLE XXXV
FLAME RETARDANT EFFICIENCY OF VBr ON PET AS A FUNCTION OF LOCATION







<u>VBR GRAFTS</u>				
OI	25.2	26.3	23.5	21.9
%F.R.	55	18.8	18.8	1.2
TGA, initial	-	138 ⁰	150 ⁰	-
Substrate	-	325 ⁰	353 ⁰	353 ⁰
Location				
	OI	21.9	21.9	
	%F.R.	1.2	2.5	
	Location			

TABLE XXXVI

Monomers Grafted

Bromine-Containing Monomers

Vinyl bromide, VBr
 Vinylidene bromide, VBr₂
 2,3-Dibromopropyl acrylate, DBPA
 2,3-Dibromopropyl methacrylate, DBPM
 2,4,6-Tribromophenyl methacrylate, TBPM
 2,4,6-Tribromophenyl acrylate, TBPA
 Tribromoneopentyl acrylate, TNPA
 2,2,2-Tribromoethyl acrylate, TBEA
 2(2,4,6-Tribromophenoxy) ethyl acrylate, TBPOEA
 Bisacrylate of 2-hydroxyethyl ether of tetrabromobisphenol
 A, BABA-50

Phosphorus-Containing Monomers

Dimethylvinylphosphonate, DVP
 Diethylvinylphosphonate, DEVP
 Dimethyl phosphonomethyl acrylate, DPA
 Dimethyl allylphosphonate, DMAP
 Bis(2-chloroethyl) vinyl phosphonate, Fyrol[®] BB
 Condensate of Fyrol[®] BB, Fyrol[®] 76
 Dimethyl 1-acetoxyvinyl phosphonate, DAVP
 Dimethyl 1-methoxyvinyl phosphonate, DMVP
 N-(Dimethylphosphonomethyl) acrylamide, NDPA
 Bis(2,3-dibromopropyl) phosphoryl-2-oxyethyl methacrylate, BDPOM

Chlorine-Containing Monomers

Vinylidene chloride, VCL₂
 1-(1,2,3,4,7,7-Hexachlorobicyclo{2.2.1}-2-hepten-5-yl)-ethene,
 "Hexa"
 Pentachlorophenylmethacrylate, PCPM

Miscellaneous Monomers

Diallylchloromethylphosphonate
 Isoprene
 Butadiene
 Acrylamide
 N-Methylolacrylamide
 Allyl Methacrylate
 N-Allylacrylamide
 Decabromodiphenyloxide

VBr and VBr₂ were courtesy of Ethyl Corporation; DBPA, DBPM, BABA-50 and TBPOEA were courtesy of Great Lakes Chemical Corp.; TBPM, TBPA, DMEVP, DPA, DMAP, DAVP, DMVP, NDPA were courtesy of Hooker Chemical Corp., and BDPOM courtesy of White Chemical Corp.

terpolymerization was also attempted. In general, grafting of these materials resulted in increased filament diameter, increased oxygen index, increased char yield, little change in tensile strength, and a large increase in elongation. The most spectacular property change due to grafting was the large increase in elongation at the yield point. The results are summarized in Tables XXXVII and XXXVIII.

Since Fyrol[®] 76 had been shown by Professor W. Walsh at North Carolina State University to have considerable potential as a radiation cureable finish for 100% cotton fabrics, attempts were made to graft this system to the PET filaments. These attempts were generally unsuccessful but better results were obtained when a reactive comonomer was added to the system. Grafting of Fyrol[®] 76 with vinylbromide in various ratios led to weight gains from 0.8 to 17%. The 17% graft analyzed for 0.5%P and 9.1%Br. It showed an increase in filament diameter from 13.5 to 15.4 μ , OI 27.9; char yield of 11.5%; tensile strength of 4.4 g/denier; and elongation of 205%.

Various ratios of Fyrol[®] 76 with acrylamide were also grafted to yield weight gains of 3.1 to 8.2%. These weight gains were achieved at the very low total dose of 10,000 rads and, thus, open possibilities for wide composition and weight gain variations.

A related commercial retardant, Fyrol[®] BB, was also grafted as homopolymer or copolymer. Homopolymer grafts from 0.8 to 3.4% have been prepared and evaluated. It is felt that with appropriate experimental modifications, higher weight gains can be achieved. In summary, the evaluation gave the following results:

filament diameter - increased uniformly with the percent weight gain from 13.9 for the 0.8% graft to 15.0 for the 3.4% graft;

OI - increased uniformly with the percent weight gain from 21.9 for the 0.8% graft to 26.3 for the 3.4% graft;

char yield - an increased char yield of at least 2% above that of control was obtained;

tensile strength - decreased slightly with increasing percent weight gain from 4.3 g/denier for 0.8% graft to 0.4 g/denier for the 3.4% graft;

TABLE XXXVII
PHYSICAL PROPERTIES OF GRAFTED PET

Fyrol BB/VBr

% Add on	OI	Char Yield	Filam. Diam.	% Elong. at yield pt.	Tenacity
4.5	27.1	1)		167	4.5 g/den
5.6	27.9	1)	14.7 μ		
6.4	28.3	1)			
8.3	29.4	1)	15.4 μ		
10.9	30.5	1)	14.7 μ	207	4.5 g/den
14.4 ²	25.5	23.7%	15.2 μ	186	5.2 g/den
15.8 ²	26.7	31.9%	15.6 μ		
23.8 ²	27.9	29.2%	15.4 μ	194	4.5 g/den

Fyrol BB/NDPA

2.3% ²	21.4	22.5%
-------------------	------	-------

Fyrol BB/NDPA/VBr

1.7%	23.5	
2.2%	24.3	21.4%
3.1%	25.5	15.9%

Fyrol BB/BDPOM

19.4% ²	30.5	24.4%
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¹Melt very "liquid"; difficult to obtain reproducible char yield data

²Fiber preswollen in sym.-ethylenedichloride.

TABLE XXXVIII

Tenacity and Elongation vs Copolymer Graft

<u>Comonomers</u>	<u>VBr: Comonomers Ratio</u>	<u>% Grafting Yield</u>	<u>Tenacity, g/den</u>	<u>Elongation Y.P.</u>
None			4.40	38
DMVP	1:1	3.9	4.73	101
DAVP	4:1	2.3	4.60	83
DPA	7:3	14.4	4.73	84
Hexa	1:1	1.8	4.40	87
Fyrol ^(R) BB	1:1	6.9	4.60	84
Fyrol ^(R) 76	2:1	17.0	4.40	78

elongation - the 0.8% graft showed a 211% elongation 1.6% graft - 183%, and 3.4% graft - 172%.

A large number of different Fyrol[®] BB/VBr compositions were also examined and found to weight gains of 0.6 to 23.8%. It was thought that this particular composition, containing phosphorus, chlorine and bromine, might exhibit an enhanced flame retardant effect since chlorine and bromine are present together in the same composition. An enhanced chlorine-bromine effect has been claimed in some antimony containing systems. For example, a 6.9% weight gain has been examined with the following results:

filament diameter	15.2 μ
OI	28.3
char yield	15.7%
tensile strength	4.6 g/den
elongation	221%

Of particular interest was the result indicating an oxygen index of 23.8 for a 7% add-on of retardant. This seemed to justify an expanded program of grafting studies and a number of experimental monomers were thus designed and synthesized by Hooker Chemicals and Plastics Corporation.

The Fyrol grafts were also compared to those obtained with vinyl bromide by use of thermal analysis. Some DSC data are reproduced in Figure 65. As it can be seen, the VBr have a melting point lower than that of virgin PET and the phosphorus grafts induce little changes in the melting point.

TGA analysis of the grafts has developed to be a very useful technique for observing the thermal behavior of the various grafted materials. Analysis of the TGA curves is outlined in Figure 66 and the initial data are summarized in Table XXXIX. From these it can be seen that the VBr grafts start decomposing at 150-176⁰C, the substrate decomposition point is lowered by about 20⁰C or more and an increased amount of char is formed in the 460-500⁰C range with the amount depending upon the % graft. This char, however, disappears above 520⁰C.

Fyrol[®] BB grafts undergo no low temperature decomposition, depress

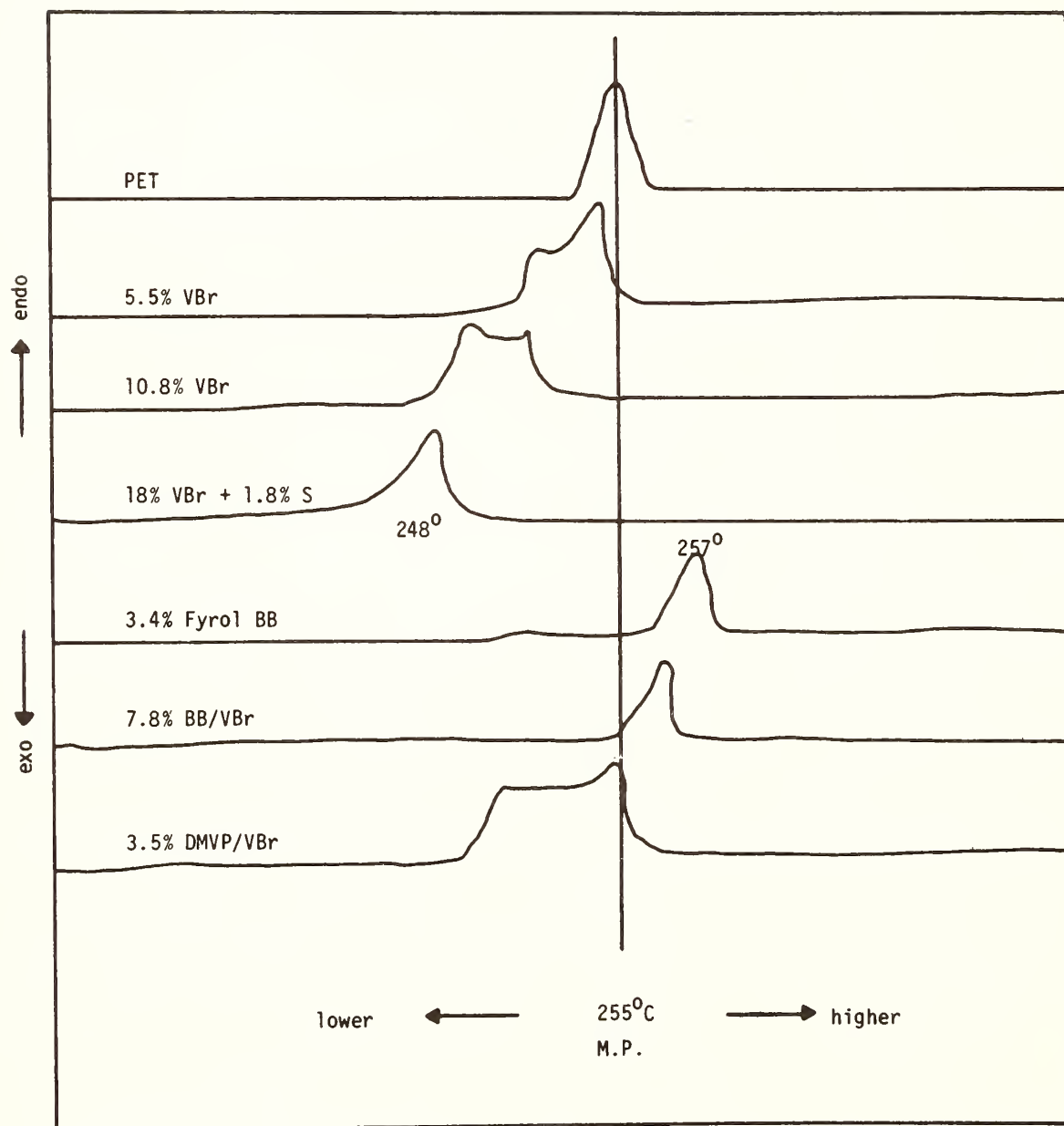


FIGURE 65. Effect of grafting on PET m.p. as measured by DSC.

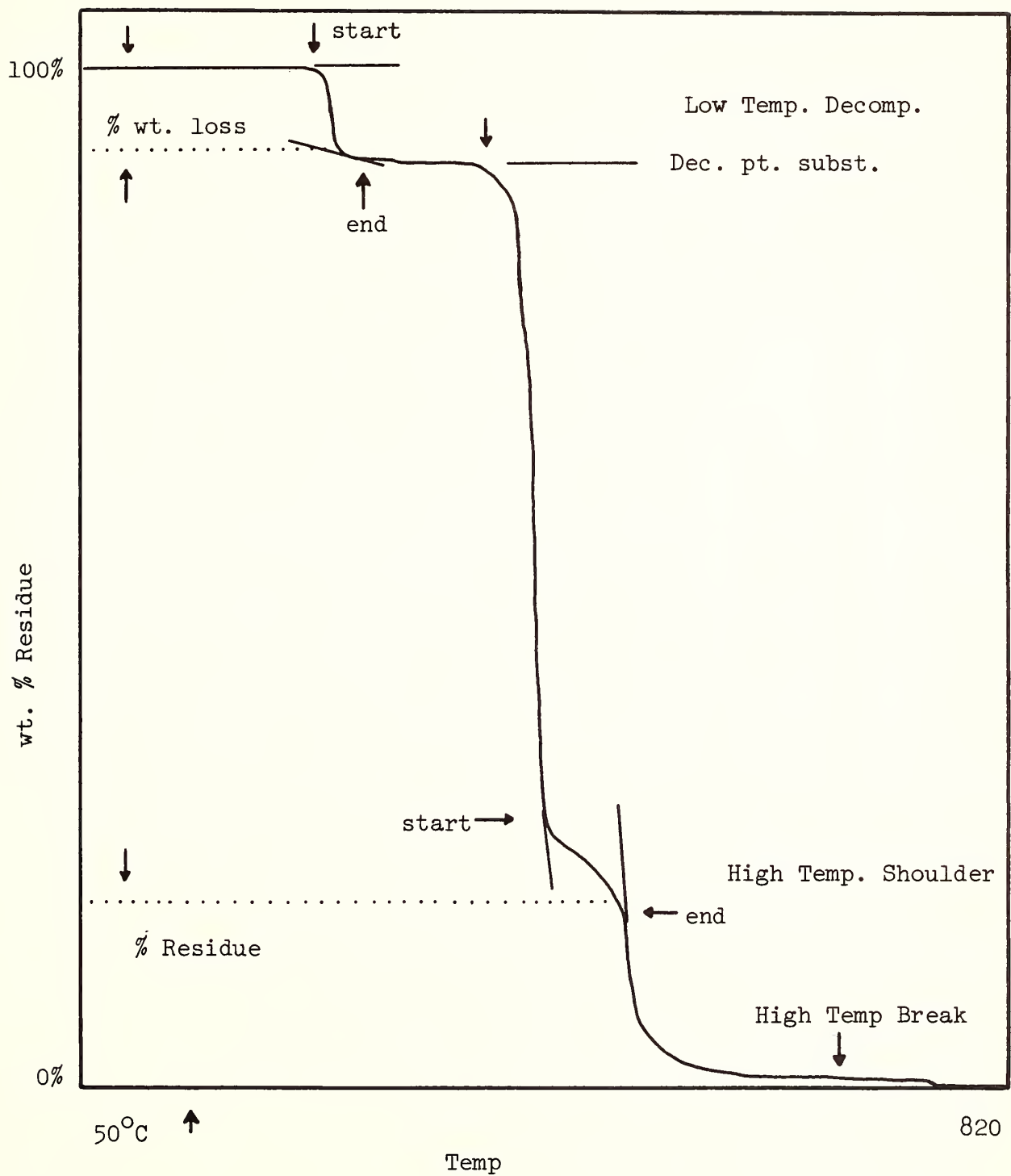


FIGURE 66. Analysis of grafted PET fiber thermogram.

TABLE XXXIX

Thermogravimetric Analysis of Grafted Polyester

<u>Low Temp. Dec.</u>		<u>Dec. Pt.</u>	<u>High Temp. Shoulder</u>		<u>High Temp.</u>	<u>No</u>
<u>Start</u>	<u>End</u>	<u>Substrate</u>	<u>Start</u>	<u>End</u>	<u>Break</u>	<u>Residue</u>
<u>Polyethylene Terephthalate</u>						
None	None	355°C	450°C	475°C 9.3% Residue		520°
<u>5.5% VBr</u>						
176°C	295° 5.5% Wt. loss	325°C	435°C	463°C 11.6% Residue		523°
<u>10.8% VBr</u>						
150°C	254°C 8.0% Wt. loss	336°C	435°C	463°C 12.5% Residue		517°
<u>18% VBr + 1.8% S (24%)</u>						
171°C	270° 14.4% Wt. loss	314°C	446°C	505°C 9% Residue PET at 505 has only 0.5% of Residue left		545°
<u>Fyrol[®] BB (3.4%)</u>						
None	None	342°C	452°C	506°C 12.2% Residue		633°

the substrate decomposition point only a little (13°C), forms more char at 500°C (12%) and require much higher temperatures (633°C) to pyrolyze away the formed char. Fyrol[®] BB-VBr grafts decompose at temperatures near 100°C , depress the substrate decomposition point by at least 30°C , and form a 12% char at 500°C which is extremely thermally stable. In one run there was still 1.9% of char left at 820°C .

Further studies were carried out on the Fyrol[®] BB system in combination with other monomers and the results are shown in Table XXXVII. If the Fyrol[®] BB was used in conjunction with VBr, the results were much better when the preswelling of the fiber prior to grafting was eliminated. Preswelling with ethylene dichloride seemed to produce a more rigid char but lower OI values. Presumably the differences observed were due to the fact that the fibers which were not preswollen have the grafting predominantly on the surface of the fiber. However, it is not clear why this should produce the observed effects.

Grafts were also attempted using DMVP and DAVP. The products from these trials gave anomalously high OI values (over 30 at add-ons as low as 4%). These values are probably not truly reflective of the flammability characteristics of the fibers since they were found to exhibit an extremely large and rapid shrinkage when exposed to the heat source. Thus, ignition in the oxygen index test was a major problem and probably contributed significantly to the anomalously high OI values. At present it is unclear whether a similar behavior would be observed if fabric rather than fiber samples were used and what implications this might have for the development of new FR treatments for 100% PET fabrics.

A variety of other monomers have been studied, both by themselves and in various combinations. Selected results obtained with the homopolymer grafts are shown in Table XL. From these data it is obvious that the efficiencies of the flame retardants vary quite widely depending upon the structure of the monomer. Also, a few of the monomers did not yield acceptable levels of homopolymerization and several techniques have been investigated in attempts to circumvent this problem. It has been found that DMVP and DAVP can be homografted to

TABLE XL

TYPICAL DATA ON GRAFTED PET FIBERS

<u>% Add-on</u>	<u>OI</u>	<u>Char Yield, %</u>	<u>Filam. Diam., μ</u>	<u>% Elong. at yield pt.</u>	<u>Tenacity, g/den</u>
<u>NDPA (postirradiation grafting)</u>					
3.0	24.7	---	14.4	263	4.06
10.4	28.3	24.0	13.5	175	3.80
<u>DMVP-VBr</u>					
1.8	26.3	1)	15.4	232	4.13
4.7	33.1	1)	14.7	265	4.73
<u>DMVP-VBr₂</u>					
0.6	31.8	1)			
<u>DMVP-VC1₂</u>					
8.3	26.7	1)	15.0	234	5.13
<u>DMVP-VBr-VC1₂</u>					
4.2	29.4	1)	13.5	246	4.80
<u>DMVP-VBr₂-VC1₂</u>					
1.7	34.1	1)	13.8	242	4.53
<u>DMVP-Acrylamide</u>					
20.4	27.9	17.1	15.0	188	4.53
<u>DAVP</u>					
1.2	23.3	1)	15.0	249	4.13
<u>DAVP-VBr</u>					
1.4	26.3	1)		248	4.93
<u>DAVP-VBr₂</u>					
1.5	29.4	18.8			
<u>DAVP-VC1₂</u>					
19.6	24.3	22.2	15.0	170	4.00
<u>DAVP-VBr-VC1₂</u>					
2.8	36.6	1)	13.9	226	4.47

TABLE XL (continued)

<u>DAVP-VBr₂-VCl₂</u>						
2.8	31.4	1)	15.0	261	4.67	
<u>DAVP-Acrylamide</u>						
8.9	28.3	21.5	13.7	224	4.73	
<u>DPA</u>						
32.9	27.1	23.6	16.5	138	3.47	
<u>DPA-VBr</u>						
14.4	27.6	26.3	15.3	219	4.73	
<u>DPA-VBr₂</u>						
14.9	28.6	16.1	14.1	214	4.73	
<u>DPA-VBr-VCl₂</u>						
18.1	27.6	18.4	15.0	223	5.00	
<u>DPA-VBr₂-BCl₂</u>						
21.4	28.6	18.0	15.0	213	4.80	
<u>BDPOM (postirradiation grafting)</u>						
10.3	29.7	1)	13.9	197	3.00	
<u>BDPOM-Fyrol[®] BB</u>						
10.5	29.4	22.3	15.0	170	5.33	
<u>BDPOM-Acrylamide</u>						
7.5	32.8		14.2	194	4.33	
<u>DBPA</u>						
9.1	27.6	17.1	13.7	152	4.67	
<u>DBPA-Fyrol[®] BB</u>						
6.4	28.3	36.0	13.9	111	4.53	
<u>DBPA-Fyrol[®] BB-VCl₂</u>						
17.8	30.5	14.5	14.5	107	4.07	
<u>DBPA-Acrylamide</u>						
71.5	31.8	17.3		150	3.20	

TABLE XL (continued)

DBPM

5.6	26.7		13.3	215	4.53
-----	------	--	------	-----	------

DBPM-Fyrol^(R)BB

5.0	30.9	23.4	13.5	145	4.20
-----	------	------	------	-----	------

DBPM-Fyrol^(R)BB-VC1₂

5.9	31.8		14.9	213	4.40
-----	------	--	------	-----	------

DBPM-Acrylamide

10.6	30.1	11.5	13.9	223	4.20
------	------	------	------	-----	------

"Hexa"

2.1	31.8	1)	13.9	213	3.20
-----	------	----	------	-----	------

"Hexa"-VBr

1.8	33.5	1)		228	4.40
-----	------	----	--	-----	------

"Hexa"-Fyrol^(R)BB

1.5	33.5	1)		234	3.47
-----	------	----	--	-----	------

"Hexa"-Fyrol^(R)BB-VBr

13.7	33.7	22.0	13.3		
------	------	------	------	--	--

TBPM

13.5	32.5	17.4	13.5	215	4.27
------	------	------	------	-----	------

TBPM-Fyrol^(R)BB

19.6	32.5	26.3	14.4	232	4.60
------	------	------	------	-----	------

TBPM-NDPA

10.0	30.9	32.2	13.5	182	4.73
------	------	------	------	-----	------

VBr

9.4	28.6	15.7		163	3.87
-----	------	------	--	-----	------

*1) The melt was extremely "liquid" and it was not possible to obtain easily reproducible char yield data.

adequate add-ons (~10%) if complexed with anhydrous ZnCl_2 before irradiation. Complexing of Fyrol[®] BB with ZnCl_2 led to more than 40% homo-graft. No doubt both ionic and free radical grafting species are generated in such a system and are responsible for the high add-ons.

High add-ons can be also achieved with monomers that do not graft easily if one utilized the gel effect. Use of allyl methacrylate, diallylchloromethyl phosphonate, and N-allyl acrylamide as the cross-linking agents in 1% concentration have been evaluated and it has been found that the methacrylate is the most efficient monomer for this purpose. Some exploratory grafting work with BABA-50 showed it to also be a very efficient gel-former. For example, at 1% it increased the Fyrol[®] BB add-on from less than 1% to more than 10%.

The results obtained from grafting trials using combination of monomers are shown in Table XL. Again, a wide range of efficiencies were found. Particularly good results were obtained when DMVP or DAVP was used in conjunction with a bromine containing monomer. The DVPM and "Hexa" systems also showed promising effectiveness in rendering the fibers flame resistant, as measured by oxygen index.

Since all of these results were obtained on fiber and yarn samples, there is a definite possibility that some of the high OI values and some of the variability observed may be artifacts of the experimental methods and thus not truly reflective of the flame retardant ability of the compounds.

By using the best PET fiber grafting technique on PET fabric, graft samples as large as 3" x 22" with VBr were obtained with add-ons above 20%. Checking one other swelling agent (DMSO) confirmed the previous experience with fibers in that organohalogen compounds are superior swelling agents and radiation sensitizers and lead to the best add-ons.

Grafting on DPA on PET fabric led to about 7% add-on. In this case apparently the best fiber grafting conditions were not the best for the fabrics.

Some VBr and DPA OI data on strips of the grafted fabrics are listed in Table XLI. The high OI for the control is an artifact of

TABLE XLI

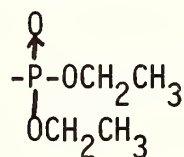
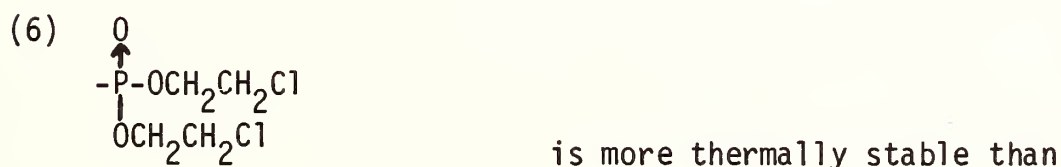
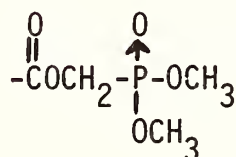
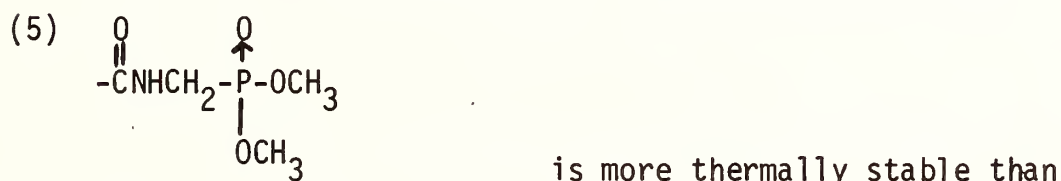
Initial Grafting Results in PET Fabric

<u>Flame Retardant</u>	<u>% Add-on</u>	<u>OI</u>	<u>Char Yield</u>
Control	0	25.2	-
Vinyl bromide	26	30.1	24.9%
Dimethylphosphonomethyl acrylate	7	25.2	-

this particular type of fabric construction.

The TGA evaluation of 26 chemically different grafts on PET fabric permitted a number of generalizations to be made. Some "structure vs decomposition point" data are summarized below:

- (1) Grafts without a decomposition point below that of the substrate are the most efficient flame retardants.
- (2) Aromatic bromine grafts are the only bromine grafts without a decomposition point below that of the substrate and is the most efficient bromine containing flame retardant.
- (3) Two bromine atoms on the same carbon atom lead to a more thermally stable graft than two bromine atoms on adjacent carbon atoms.
- (4) One aliphatic bromine atom leads to a more thermally stable structure than two bromine atoms on adjacent carbon atoms.



- (7) Two isolated chlorine atoms (as compared to perchlorocyclopentadiene structure) on the same carbon atom lead to a thermally unstable structure.
- (8) Perchlorocyclopentadiene structure is a relatively thermally stable structure and as a result is a very efficient flame retardant for PET fiber.

In the bromine graft series the apparent thermal stability of the

graft and its flame retardant efficiency may be related to the aliphatic hydrogen-bromine ratio (see Table XLII); the lower the ratio the higher the efficiency. The most efficient flame retardants appear to be those with no low decomposition point, see Table XLIII. The amide vs. ester and bromine graft structure-thermal stability correlations agree with pertinent data in the literature, see Table XLIV.

2.c. Topical Treatments Utilizing Conventional Fixation Methodology:

Although the problem of devising flame retardant treatments for 100% PET fabrics was itself outside of the scope of this project, a few preliminary experiments were carried out on 100% PET to provide a background for the subsequent work with the blends. In one study the feasibility of applying flame retardants to the polyester by dyeing techniques was evaluated.

In an alternate approach to the treatment of PET fabrics, heat cureable and ammonia cureable phosphonium derivatives were examined. Of these, only the precondensates of tetrakis-hydroxymethylphosphonium sulfate (THPS[®]) produced finishes which appeared to have significant effect on the PET flammability. Of particular interest was the condensation product formed by heating THPS[®] with trimethylphosphoramidate (MCC-100[®]) and trimethylmelamine at reflux for 16-20 hours. When this material was applied to 100% PET with urea in a pad-dry-NH₃ cure process under laboratory conditions, the results shown in Table XLV were obtained. The fact that all of the samples exhibited char length of less than 5 in. when burned without support whereas the highest level burned completely when stitched with three fiberglass threads may indicate that even though the treatments result in increased levels of char production the retardant is acting predominantly by lowering the melt viscosity of the PET. This would not be unexpected in view of the known decomposition of phosphonium compounds to acid anhydrides. It would also be consistent with the results obtained with the DAP treated PET described earlier. It would also be consistent with an observation that small amounts of H₂SO₄ will allow PET to

TABLE XLII

Flame Retardant Efficiency as a Function of Thermal Stability

Compound	Aliphatic H/Br	Dec. Pt.	OI/1%Br
$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{O}-\text{C}_6\text{H}_2(\text{Br})_2-\text{Br} \end{array}$	0	303°C	1.5
$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{O}-\text{CH}_2\text{CH}_2\text{O}-\text{C}_6\text{H}_2(\text{Br})_2-\text{Br} \end{array}$	0	-	1.2
$\begin{array}{c} \text{Br} \\ \\ \text{CH}_2 \\ \\ -\text{COCH}_2-\text{C}-\text{CH}_2-\text{Br} \\ \\ \text{CH}_2 \\ \\ \text{Br} \end{array}$	0	300°C	-
$\begin{array}{c} \text{O} \\ \parallel \\ -\text{COCH}_2-\text{C}-\text{Br} \\ \\ \text{Br} \end{array}$	2/3	220°C	1.1
$\begin{array}{c} \text{BR} \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{BR} \end{array}$	1	204°C	1.0
$\begin{array}{c} -\text{CH}_2-\text{CH}- \\ \\ \text{BR} \end{array}$	2	150°C	0.5
$\begin{array}{c} -\text{CH}_2-\text{CH}-\text{CH}_2 \\ \quad \\ \text{Br} \quad \text{Br} \end{array}$	2.5	132°C	(0.2)
$\begin{array}{c} -\text{CH}_2\text{CH}-\text{CH}-\text{CH}_2- \\ \quad \\ \text{Br} \quad \text{Br} \end{array}$	3	127°C	-
$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}-\text{CH}-\text{CH}_2- \\ \quad \\ \text{Br} \quad \text{Br} \end{array}$	4	122°C	-

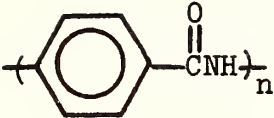
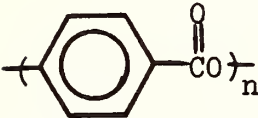
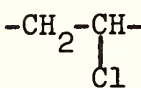
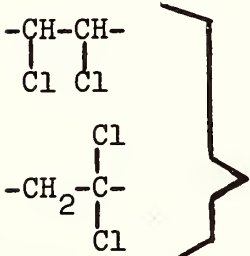
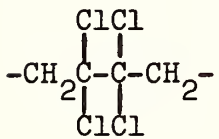
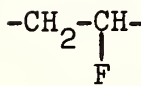
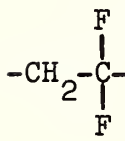
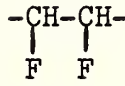
TABLE XLIII

GRAFTS WITH NO LOW TEMPERATURE DECOMPOSITION POINT

<u>Monomer</u>	<u>Substrate Dec. Pt.</u>	ΔT <u>Substrate Dec. Pt.</u>
Control PET	355 ^o C	-
TBPM	303 ^o	52 ^o C
Hexa	325 ^o	30 ^o
NDPA	325 ^o	30 ^o
Fyrol ^(R) BB	342 ^o	13 ^o

TABLE XLIV

MAXIMUM STABILITY OF POLYMER REPEAT UNITS*

	$T_{\text{dec}} (\text{N}_2)$	
	600°	
	480°	
	260°	$V_{\text{br}} (138^\circ \text{C})$
	215-220°	$V_{\text{br}} (110-127^\circ; 204^\circ)$
	320°	
	386°	
	430°	
	365°	

* Reference 71.

TABLE XLV

Effect of Phosphonium Precondensates on PET Flammability

<u>% Add-on</u>	<u>Average Initial Char Length</u>	<u>Average Char Length After 50 Launderings</u>
22.4 ⁽¹⁾	1.0 in.	-
10.2 ⁽²⁾	2.9 in. (6.4 sec.) ⁽³⁾	4.1 in. (7.0 sec.) ⁽³⁾
7.8 ⁽²⁾	3.2 in. (5.1 sec.) ⁽³⁾	4.3 in. (6.4 sec.) ⁽³⁾
4.5 ⁽²⁾	2.8 in. (4.9 sec.) ⁽³⁾	2.5 in. (4.2 sec.) ⁽³⁾

(1) Prepared by Clemson

(2) Prepared by United Merchants & Manufacturers

(3) Average afterflame time; at each level, at least one sample exhibited an afterflame time of greater than 10 sec.

achieve very small char lengths.

STUDIES ON POLYESTER/COTTON BLENDS

In order that the results from all of the participating laboratories might be comparable, a single lot of fabric was chosen to be used as the standard for all of the ETIP work. This was a 4.2 oz. 50/50 poplin purchased from Dan River Mills and prepared by the Old Fort Finishing Plant of United Merchants. Unless otherwise specified, all results are reported on this standard ETIP fabric.

FLAME RETARDANT SYSTEMS BASED ON PHOSPHORUS ALONE

Based on the knowledge that phosphorus may exhibit flame retardant action in both the fuel generating and fuel consuming processes, it should be possible to design organophosphorus compounds capable of producing both effects on polyester/cotton blends.

1. Antiblaze[®] 19

One organophosphorus retardant which would appear to meet this criterion is Antiblaze[®] 19 produced by Mobil Chemical Company. The literature indicates that this material is a mixture of cyclic phosphonates, probably a dimer and trimer, with closely related structures but different volatilities, and having a total phosphorus content of 21%.

A series of 65/35 and 50/50 polyester/cotton blend fabrics was treated with this retardant and evaluated by the 45⁰ angle subjective burn test. The results of these tests along with the corresponding oxygen index values are given in Table XLVI. As might be expected from the previous discussion of testing methodology, there seems to be little correlation between the observed oxygen index values and the behavior of the fabrics on the 45⁰ angle burn test using edge ignition with a wooden kitchen match. The 45⁰ angle test, as carried out, should constitute an extremely severe test. Those fabrics which are designated as "difficult to ignite" resist ignition for periods as long as 20 seconds, indicating that they should be more than satisfactory for passing most vertical burn tests. Because it seems likely that the most important factor in causing this discrepancy in results is one of geometry, these samples were also evaluated by bottom ignition oxygen

TABLE XLVI
FLAMMABILITY OF BLENDS TREATED WITH ANTIBLAZE[®] 19

<u>%P⁽¹⁾</u>	<u>OI</u>	<u>45°Burn</u>
3.0 ⁽²⁾	25.0	Does not burn
2.2 ⁽²⁾	23.0	Difficult to ignite
1.4 ⁽²⁾	22.2	Burns
3.3 ⁽³⁾	25.5	Does not burn
2.2 ⁽³⁾	23.8	Difficult to ignite
1.5 ⁽³⁾	22.5	Burns

¹Calculated assuming Antiblaze[®] 19 21%P.

²On 65/35 polyester/cotton blend

³On 50/50 polyester/cotton blend

index. The BOI values were much more consistent with the vertical test results than the OI values. Thus it would appear that Antiblaze[®] 19 should be particularly effective in vertical upward burning situations.

Because of the rather unusual activity demonstrated by Antiblaze[®] 19, fabrics containing this material have been evaluated more thoroughly than would normally be done with compounds of undesignated structure. A series of 50/50 cotton/polyester blends treated at five levels of Antiblaze[®] 19 ranging in phosphorus content from 0.94 to 3.20 have been evaluated by isoperibol calorimetry and the results are tabulated in Table XLVII. The char yields, heat evolution and rates of heat evolution from these samples clearly indicate that this particular flame retardant does not exert its effect in any manner similar to those previously studied. For a phosphorus content of 3.20%, char yields were increased only from 6.6% to 17.4% and the heat release was reduced by about 500 calories from the control. This compares to char yields of approximately 18% and a heat release reduction of almost 800 cal/gm for a 50/50 blend treated with a phosphoric acid to a level of 1%P. It was also noted that the behavior of fabrics treated with Antiblaze[®] 19 was very susceptible to changes in burning environment. In the relatively high air-flow of the isoperibol calorimeter, fabrics burned which would not burn in open air 45° angle test. This may indicate some type of physical effect rather than chemical retardation. Unfortunately the sources of these discrepancies have not been found. Further work with this material was abandoned after repeated attempts to fix the retardant to produce a durable finish on the 50/50 blend.

TABLE XLVII

ISOPERIBOL CALORIMETRY RESULTS FROM ANTIBLAZE[®] 19TREATED 50/50 POLYESTER/COTTON BLEND

%P	%R	Rate. cal/sec-cm	- ΔH_1 , cal/gm
0.94	9.1	57.5 \pm 2.2	2609
1.20	9.3	59.6 \pm 4.3	2468
1.60	10.1	55.1 \pm 4.3	2446
2.20	11.9	47.8 \pm 0.4	2384
3.20	17.4	51.0 \pm 4.3	2298
control	6.6	62.0 \pm 1.8	2767

2. N-methylol-3-(diphenylphosphinyl) Propionamide

Another system containing only phosphorus, which exhibits interesting flame retardant characteristics, is that based on N-methylol-3-(diphenylphosphinyl)-propionamide (MD3P), a compound synthesized at Clemson. When this material was evaluated by oxygen index in an unfixed form (simply impregnated into the fabric by padding), the results shown in Figure 67 were obtained. The OI values obtained on 100% polyester were surprisingly large as compared to those obtained on 100% cotton fabric. Not only were the polyester values large, but they seemed to pass through a maximum at about 13% MD3P. The reason for this is not clear at present. On the two blend fabrics, the flame retardant efficiency as reflected by oxygen index was slightly greater than on 100% cotton, but not nearly so great as on the polyester. Additionally, it was noted that the efficiency on the 50/50 blend was essentially the same as that on the 65/35. Char values achieved with this retardant were measured in the normal manner for static oxygen bomb measurements, and also from runs made on the isoperibol calorimeter. With 100% cellulosic material (Figure 68), the two techniques gave essentially the same char yields, whereas Figure 69 shows that with the 50/50 blend the char obtained in the vertical burnings for static oxygen bomb calorimetry were considerably larger than those obtained from the isoperibol. Presumably this difference is a result of the sample folding back on itself as burned in an unconstrained configuration. The values obtained for the samples held on the pin frame in the isoperibol calorimeter may be more reflective of the actual activity of the flame retardant. There is, however, the alternate interpretation that the flame retardant becomes less efficient in the flowing air environment of the isoperibol calorimeter in a manner similar to that previously observed with fabrics treated with Antiblaze[®] 19. In either case, the conclusion is reached that the material exhibits some condensed phase activity and thus promotes some char formation, but the magnitude of this activity is not large compared to other systems known to be completely active in the condensed phase.

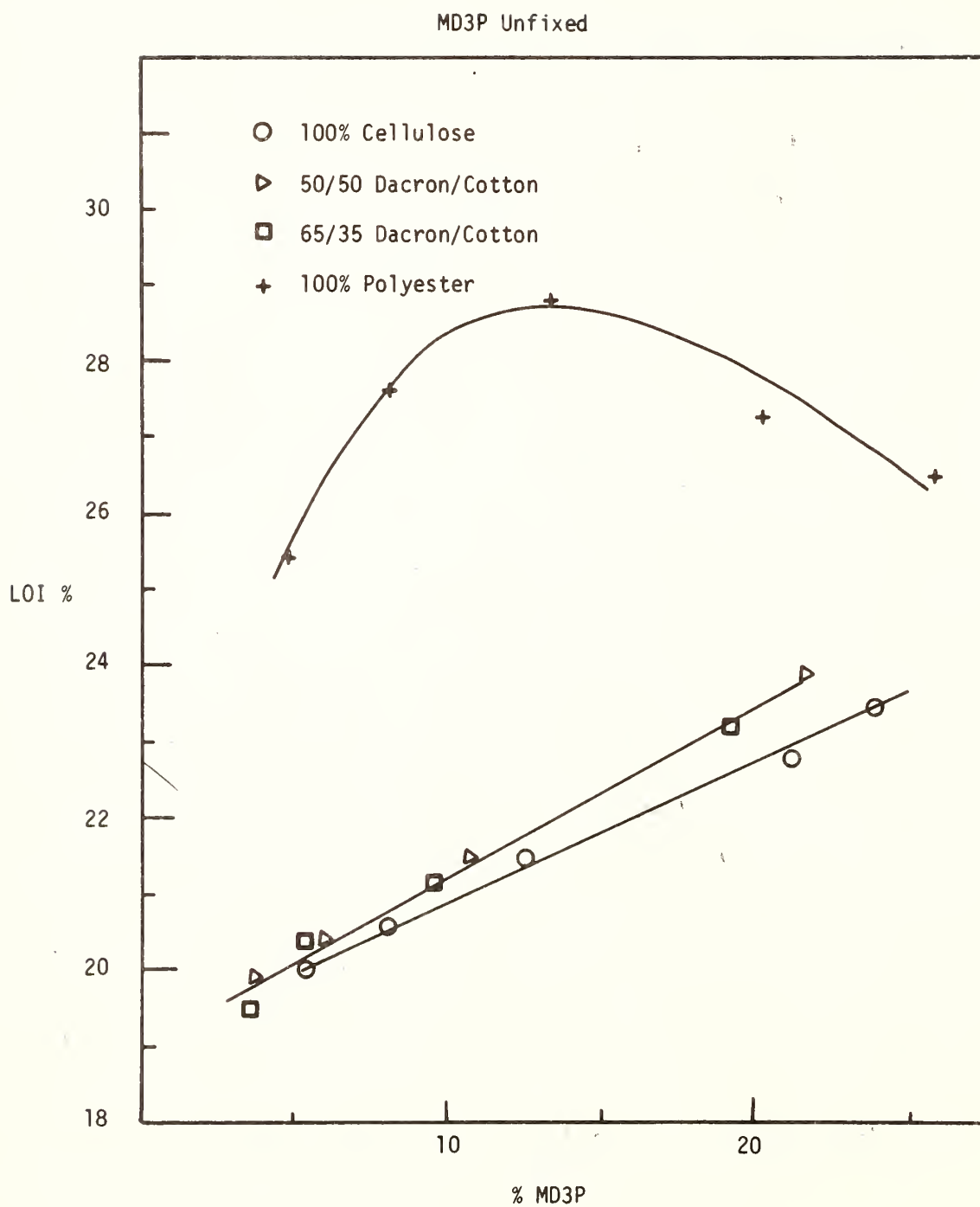


FIGURE 67. OI as a function of % MD3P (unfixed).

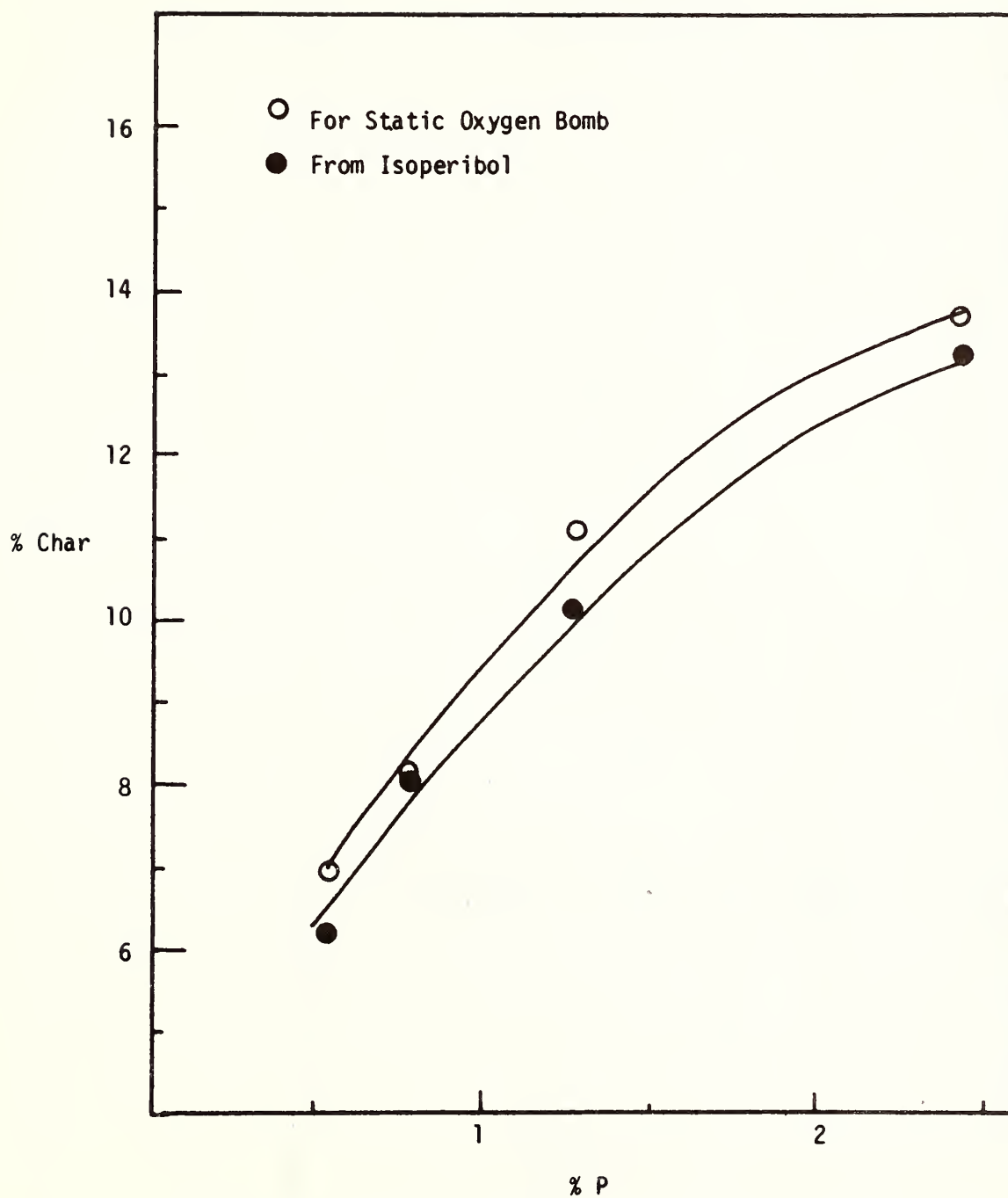


FIGURE 68. Char formation as a function of MD3P (unfixed) on cotton.

50/50 Dacron/Cotton with MD3P Unfixed

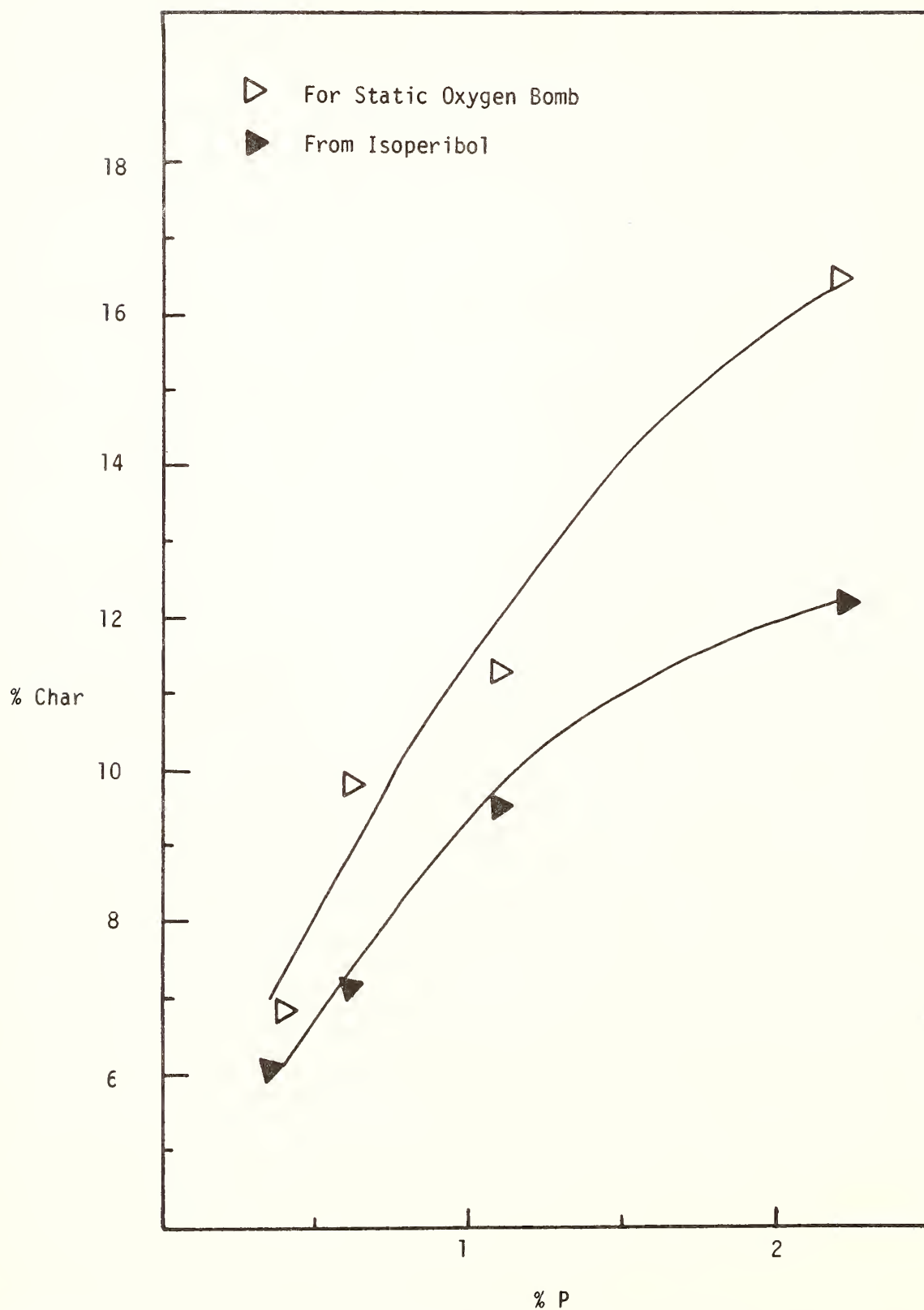


FIGURE 69. Char formation as a function of MD3P (unfixed) on 50/50 PET cotton.

The results of the static oxygen bomb calorimetry on the fabrics containing the unfixed MD3P are shown in Figures 70 and 71. The high values obtained in both the $Y/(1-X)$ and the $\Delta H_2/(\Delta H_C^0)_F$ treatments of the data are easily interpretable in terms of relatively minor contributions to the flame retardant activity by condensed phase reactions.

Isoperibol calorimetry produced the results shown in Tables XLVIII and XLIX. The ratio of ΔH_1 to ΔH_2 , which is a measure of the incomplete combustion of the fuel gases liberated on pyrolysis of the fabric, indicates an increase in the unburned vapors with increasing amounts of unfixed MD3P. This suggests vapor phase activity.

The MD3P was also studied in a fixed form. The retardant was applied with an Aerotex[®] 23 resin and a phosphoric acid catalyst using a drying of five minutes at 60°C followed by curing at 150°C for two minutes. After fixing, the OI values for the treated blends were increased, whereas those for the 100% cotton fabric were essentially the same as with the unfixed form (Figure 72). Based on the hand of the fabric, it would seem that the unfixed samples have significant amounts of surface treatments on the blends, whereas penetration is possible in the case of 100% cellulose. With the materials present in an unfixed form the flame retardant is probably released ahead of the flame front, decreasing its efficiency. Fixation reduces the volatility of the material and retards its volatilization so that more effective vapor phase action can be achieved. Such an interpretation would seem to be consistent with the results of the subjective 45° angle burning evaluations. In these tests, the flame retardant was found to be much more efficient than would be predicted on the basis of OI values. As in the case of Antiblaze[®] 19, it was necessary to resort to bottom burning oxygen index (BOI) to evaluate the flammability of these samples (see Table IV).

Calorimetric evaluation of the fabrics has also been carried out. Samples of 50/50 polyester/cotton treated with the MD3P in a fixed form would not support combustion at levels of 25% or greater. The char for the static oxygen bomb was prepared by holding a match under the fabric until charring was completed. In the isoperibol, the sample containing

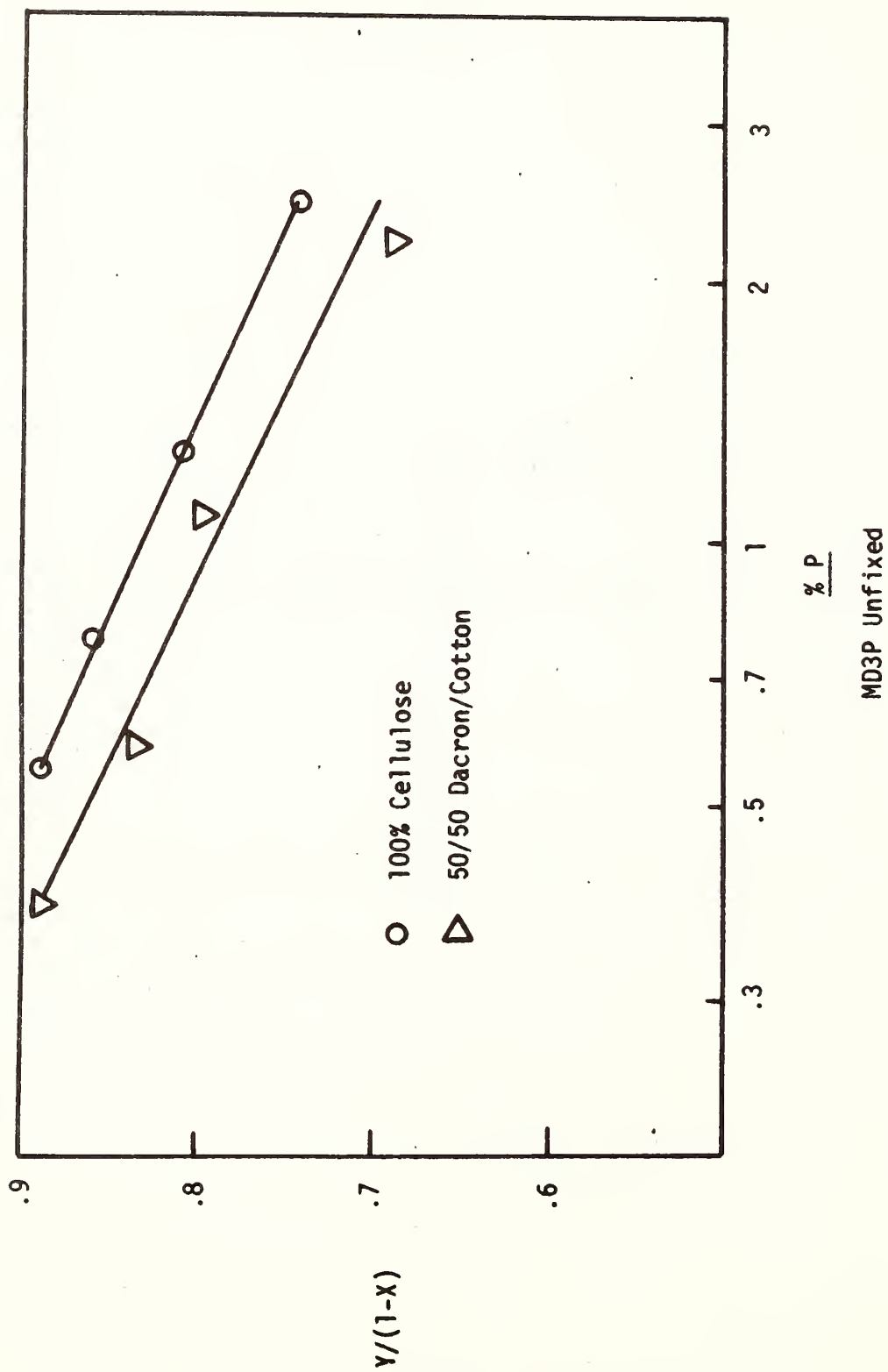


FIGURE 70. Comparison of the flame retardant efficiency of MD3P (unfixed) on cotton and 50/50 PET cotton.

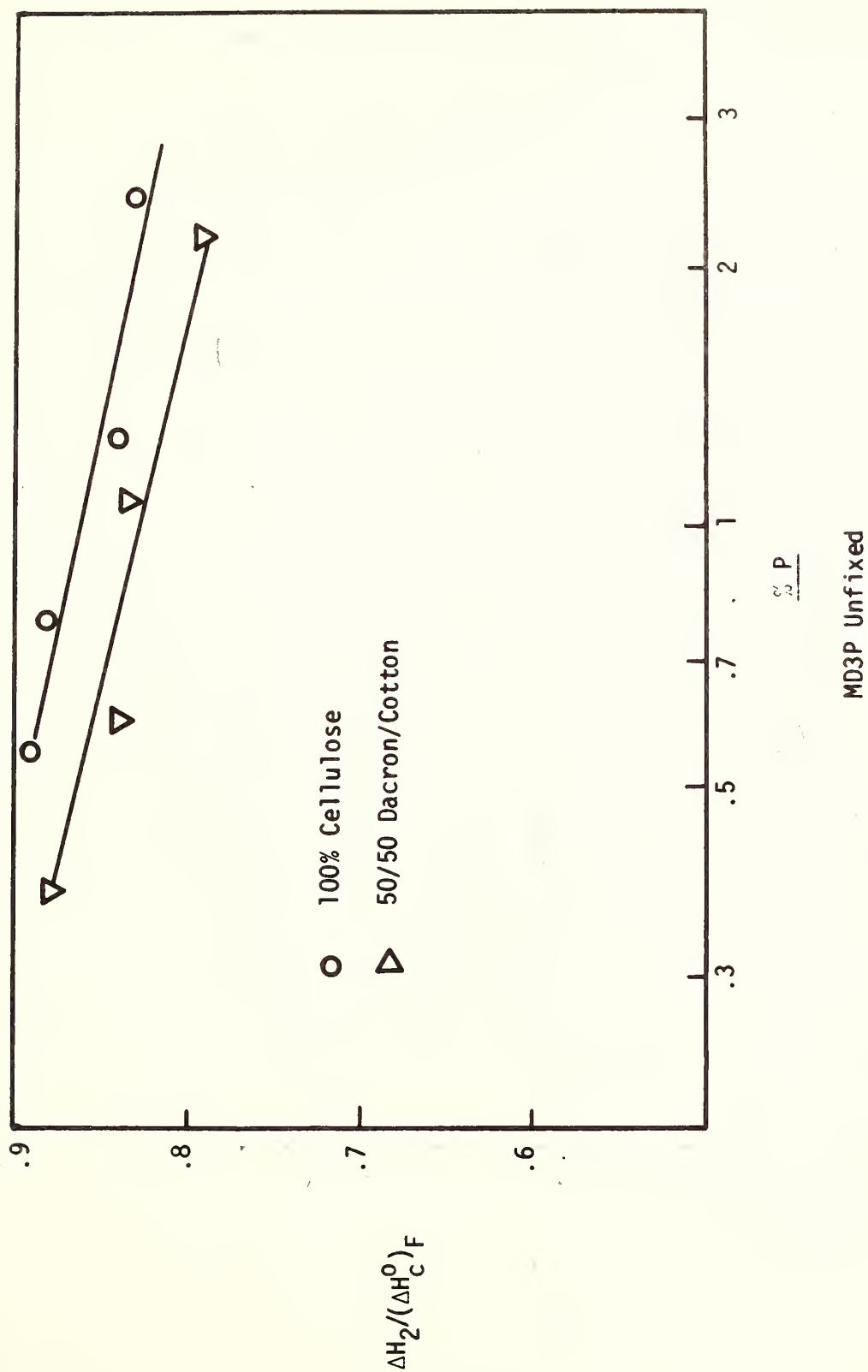


FIGURE 71. $\Delta H_2/(\Delta H_C^0)_F$ for MD3P (unfixed) on cotton compared to 50/50 PET/cotton.

TABLE XLVIII
100% COTTON FABRIC TREATED WITH MD3P (UNFIXED)

<u>%MD3P</u>	<u>$-\Delta H_2$, cal/gm</u>	<u>$-\Delta H_1$, cal/gm</u>	<u>$\Delta H_1/\Delta H_2$</u>
23.6	3650	1992	.55
12.9	3395	2219	.65
7.9	3433	2447	.71
5.2	3456	2506	.73

TABLE XLIX
50/50 PET/COTTON TREATED WITH MD3P (UNFIXED)

%MD3P	$-\Delta H_2$, cal/gm	$-\Delta H_1$, cal/gm	$\Delta H_1/\Delta H_2$
21.6	3848	2099	.55
10.6	3862	2345	.61
5.9	3878	2466	.64
3.7	3964	2593	.65

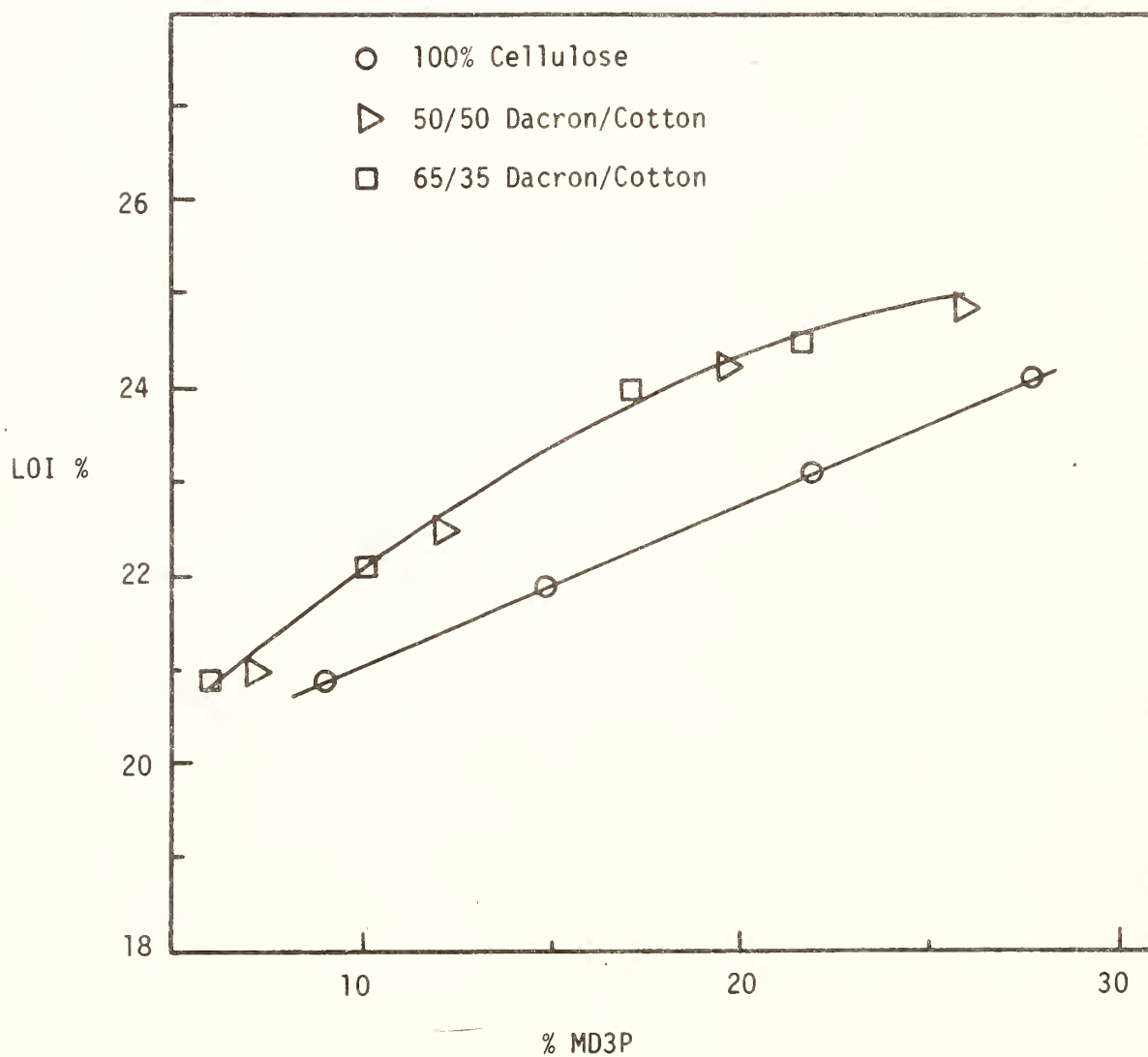


FIGURE 72. OI of MD3P (fixed) on PET/cotton blend fabrics.

26.6% MD3P did not burn completely and left a char residue of 50.1%. It should also be noted that 50/50 blend fabrics containing 19.6% MD3P were extremely difficult to ignite in open air burning, but would burn the entire length after ignition. They would undoubtedly pass any of the standard vertical tests using 3 or 12 second ignition. Samples of 100% cotton with 27.7% MD3P behaved in manner similar to that of the 50/50 blend with 19.6% MD3P

There are other indications which support this suggestion that the entire mechanism of action may change when MD3P is fixed. Figures 73 and 74 show the char yields achieved as a function of the phosphorus content. In the case of the fixed retardant the chars increase significantly above 2%P, whereas the unfixed system shows a slight decrease in this area. As would be expected, the dependence of $Y/(1-X)$ on $\log \%P$ exhibited a similar effect (Figure 75). The unfixed reagent produced a low order of dependence whereas in the fixed form a steep slope similar to that found with typical effective condensed phase retardants was found. This behavior was also reflected in the values of $\Delta H_1/\Delta H_2$ as shown in Tables L and LI.

In an attempt to understand the origin of this anomalous behavior, elemental analysis has been carried out on the chars from the burned samples. With the unfixed retardant on both fabrics, the phosphorus retention was low and showed no apparent correlations with initial retardant add-on. On the 100% cellulose fabric, the nitrogen retention was only slightly higher than that of phosphorus; but with the 50/50 blend, the nitrogen was $1\frac{1}{2}$ to 2 times that of the phosphorus retention. The fixed samples showed higher retention than the unfixed. The much higher retention observed in both cases for the samples with the highest weight add-on compares with the unusually large char yield and low $Y/(1-X)$ values observed. For both fabrics, nitrogen retention was $1\frac{1}{2}$ to 2 times that of phosphorus.

The results of TGA studies in this system agree with the data obtained in the previous studies. The unfixed samples show very little residue at 500°C and the material seems to exhibit no pronounced catalytic effect on the polymer decomposition. These results are presented

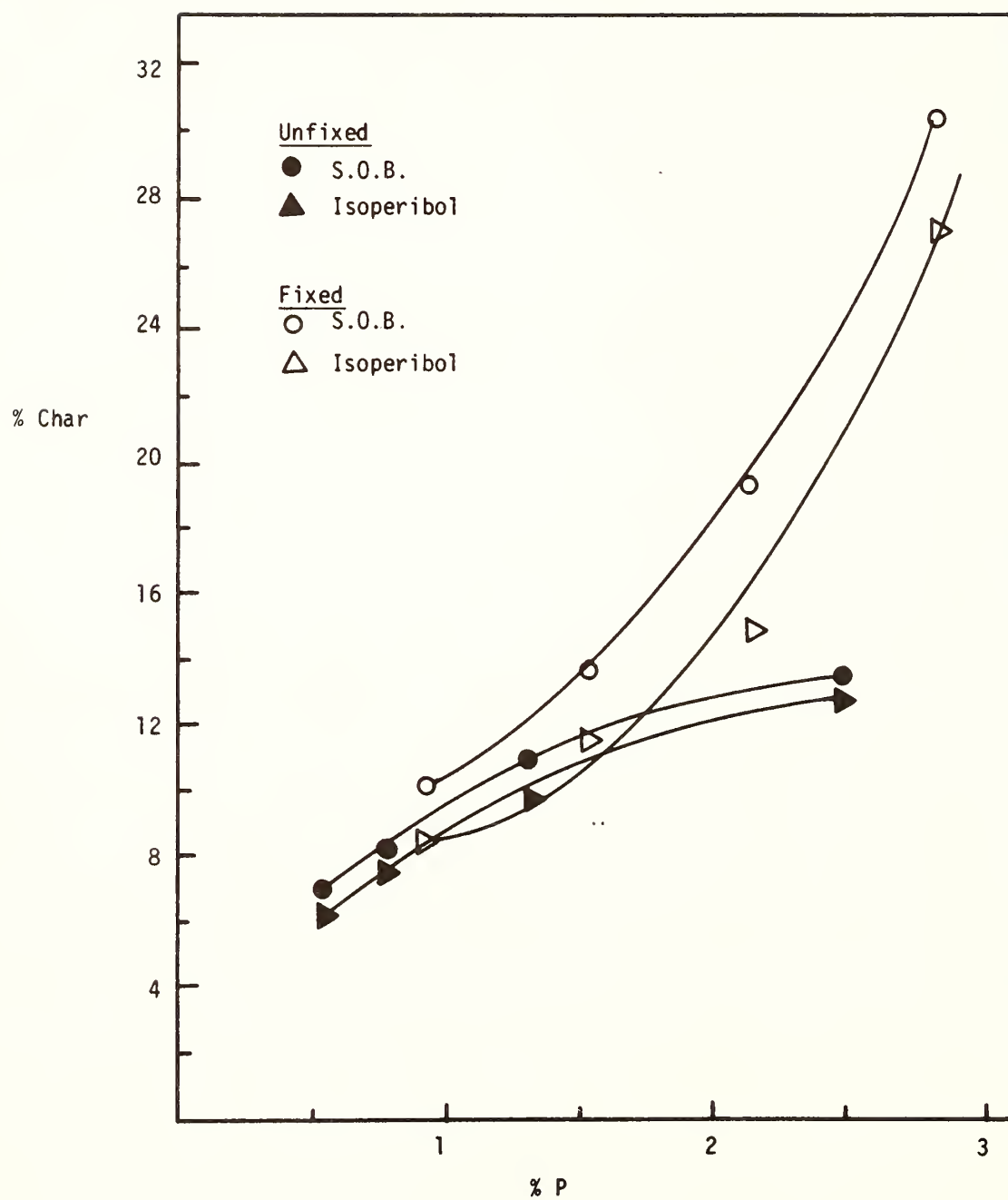


FIGURE 73. Effect of fixation on chars from MD3P treated cotton.

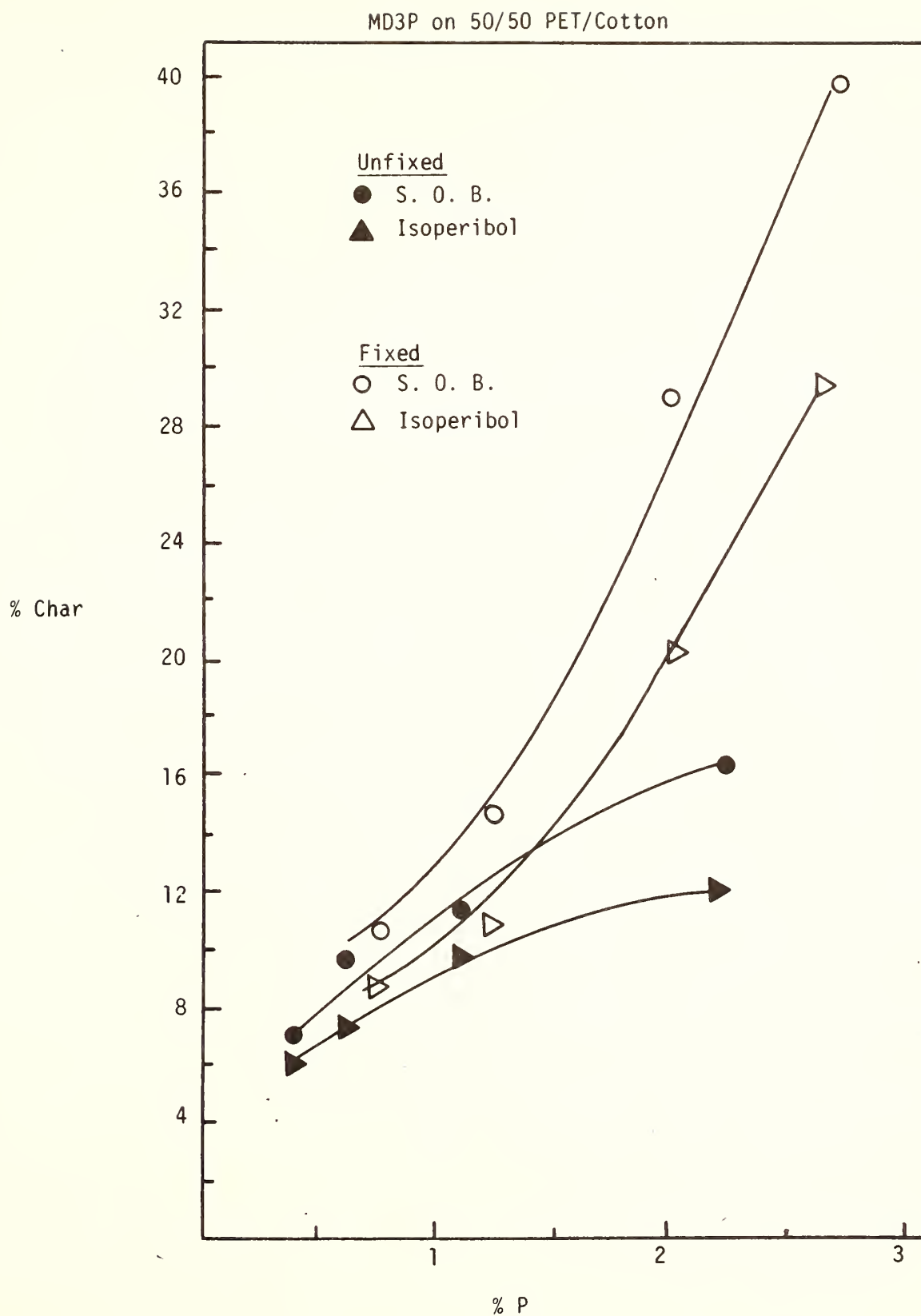


FIGURE 74. Effect of fixation on chars from MD3P treated 50/50 PET/cotton.

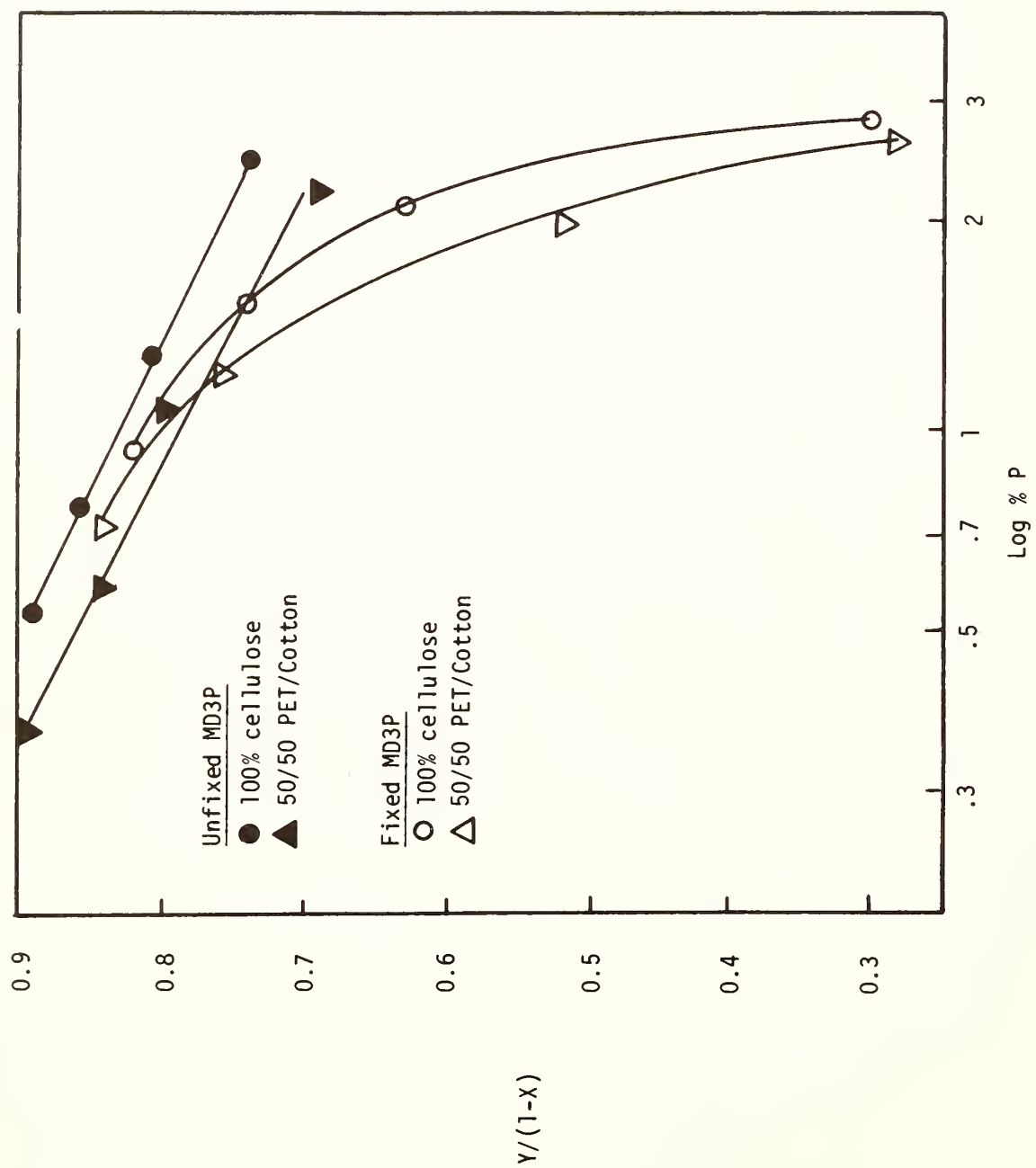


FIGURE 75. Effect of fixation of MD3P on its flame retardant efficiency.

TABLE L

100% COTTON FABRIC TREATED WITH MD3P (FIXED)

<u>%MD3P</u>	<u>$-\Delta H_2$, cal/gm</u>	<u>$-\Delta H_1$, cal/gm</u>	<u>$\Delta H_1/\Delta H_2$</u>
27.74	2578	1920	.74
20.97	3173	2142	.68
14.95	3299	2225	.67
9.11	3371	2355	.70

TABLE LI
50/50 PET/COTTON TREATED WITH MD3P (FIXED)

<u>%MD3P</u>	<u>-ΔH_2, cal/gm</u>	<u>-ΔH_1, cal/gm</u>	<u>$\Delta H_1/\Delta H_2$</u>
25.90	2584	1999	.77
19.59	3107	2099	.68
12.09	3766	2246	.60
7.15	3928	2330	.60

in Figures 76 and 77. The weight loss which occurs between 140° and 210° corresponds with weight loss observed in the case of pure MD3P as shown in Figure 76. The weight loss for MD3P at about 85° occurs at the melting point and is probably due to solvent trapped during the re-crystallization process. This has also been indicated by NMR. The weight loss which occurs between 140° and 210° agrees with calculations for loss of formaldehyde.

Analysis by TGA of 100% cellulosic material with the MD3P in fixed form (Figure 78) shows no significant modification except at the highest phosphorus add-on where a large change is observed in both decomposition temperature and char yield. The blend fabrics with the fixed reagents (Figure 79) showed this same large decrease in initiation temperature at the two highest levels of phosphorus incorporation. There is no apparent correlation between percent phosphorus and the amount of char residue with the blends; but the change in slope during decomposition, which is likely due to a change from cellulose to PET decomposition, occurs at a lower weight loss as the percent phosphorus increases.

Differential thermal analysis of the cotton fabric containing the unfixed reagent shows a decrease in the endotherm nadir attributable to the cellulose decomposition from 375° to 340° as the phosphorus content increases. The 50/50 blend fabrics exhibit no observable change in the nadir of the endotherm. In these materials a shoulder appears 10° to 15° below the nadir which could be caused either by decomposition of the MD3P or by reaction with the cellulose. The DTA of neat MD3P has four endotherms with nadirs at 95° , 180° , 365° and 425°C . The first three endotherms are attributable to the melting point, the probable formaldehyde loss and the large weight loss observed by TGA. The origin of the endotherm at 425° is not known.

Fixed MD3P on 100% cotton fabric shows no significant changes in DTA except in the case of the samples containing 2.8% phosphorus. This is in keeping with the TGA results. In the case of the 50/50 blend fabric, the nadir of the decomposition endotherm decreases to approximately 300° for samples containing 2.0 or 2.6% phosphorus. Thus it would seem

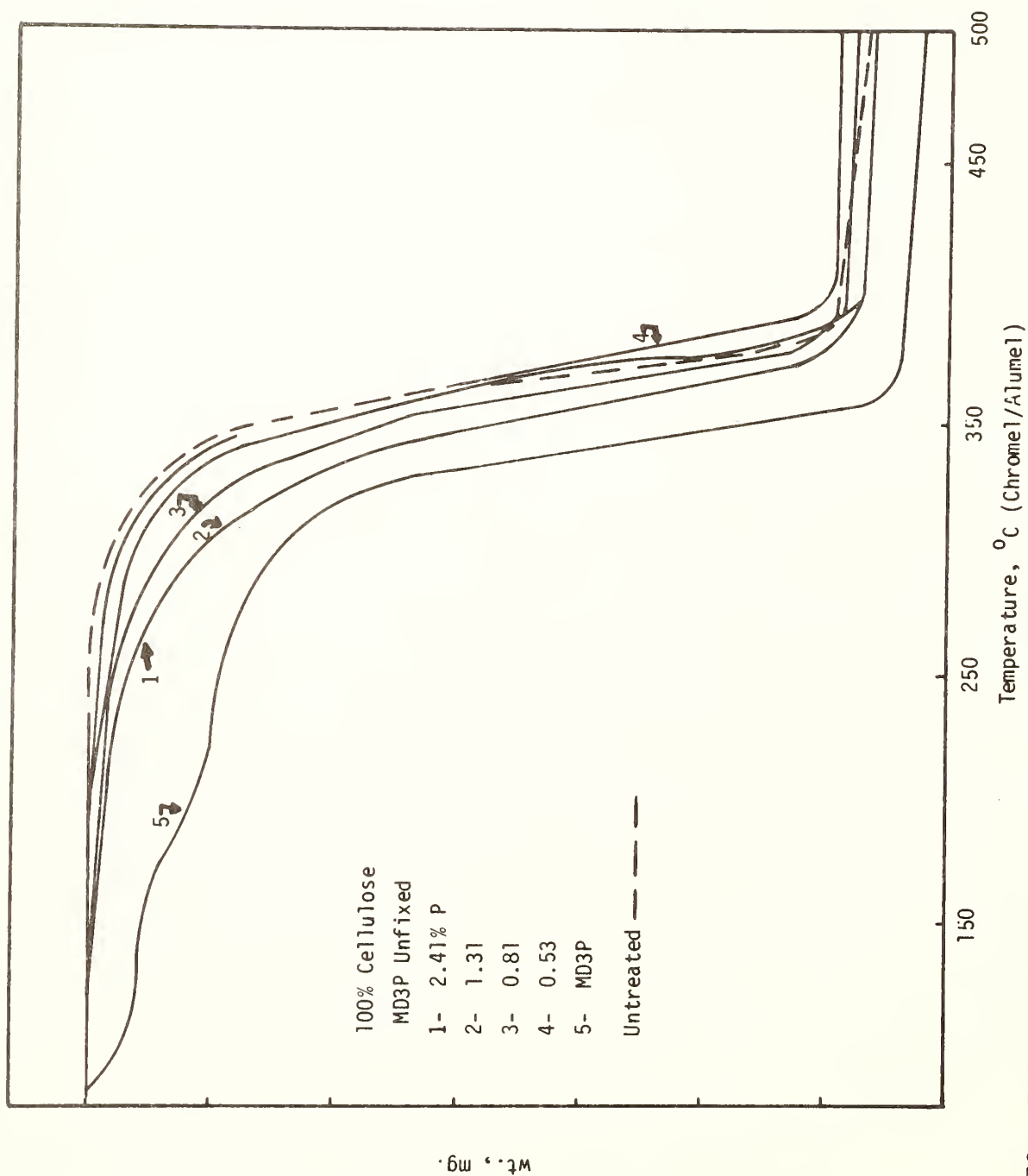


FIGURE 76. TGA of MD3P (unfixed) on cellulose.

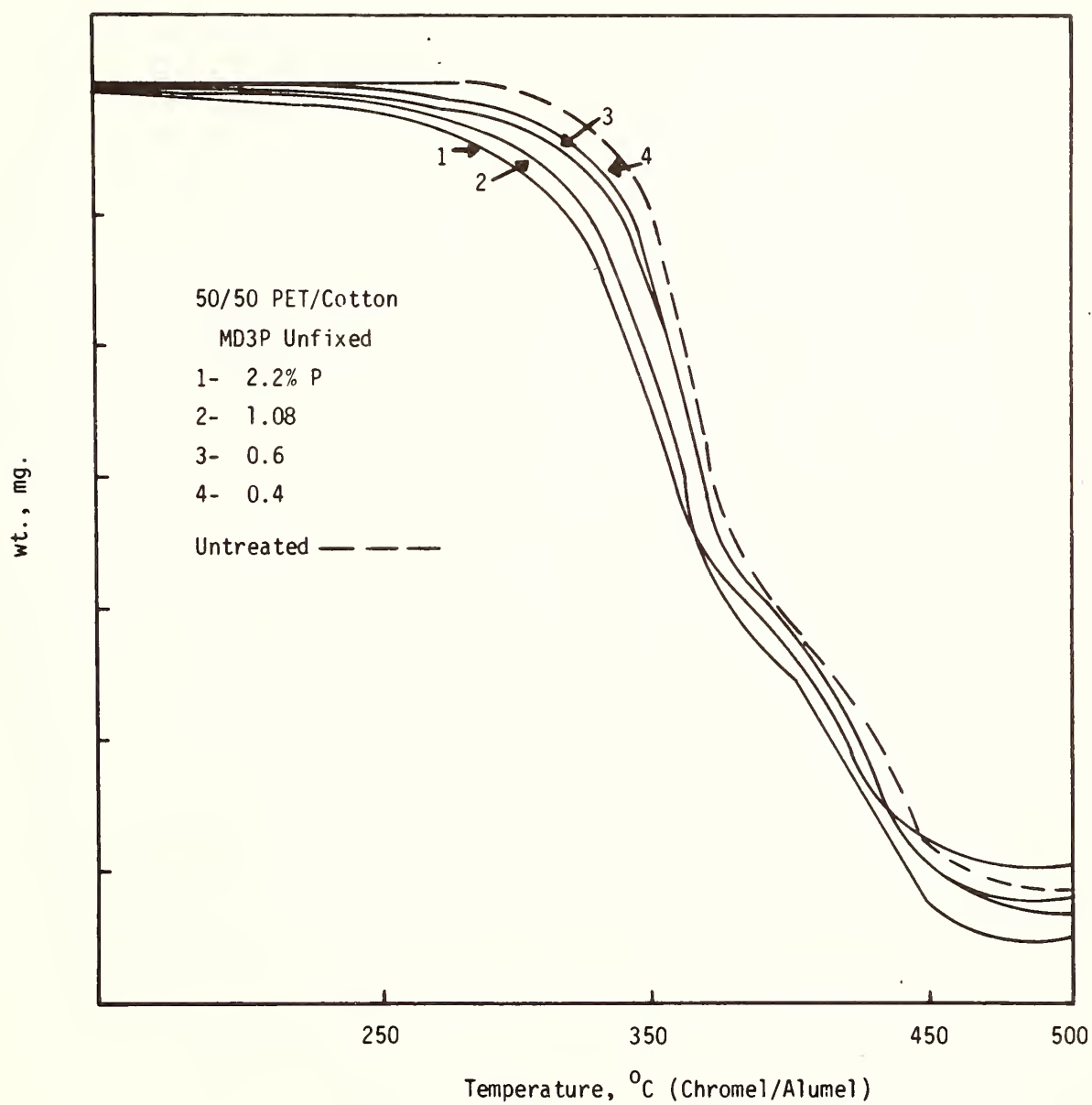


FIGURE 77. TGA of MD3P (unfixed) on 50/50 PET/cotton.

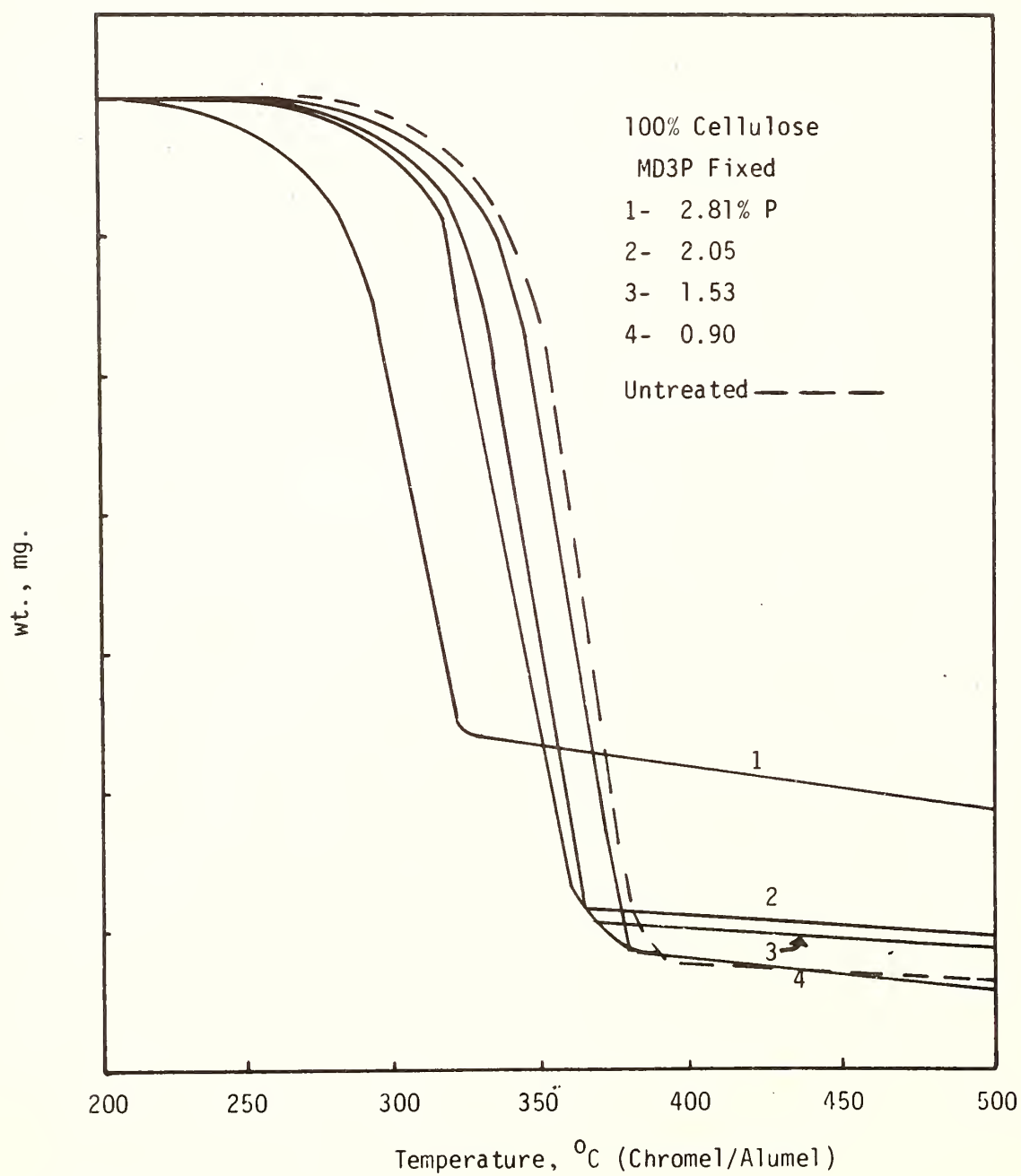


FIGURE 78. TGA of MD3P (fixed) on cotton.

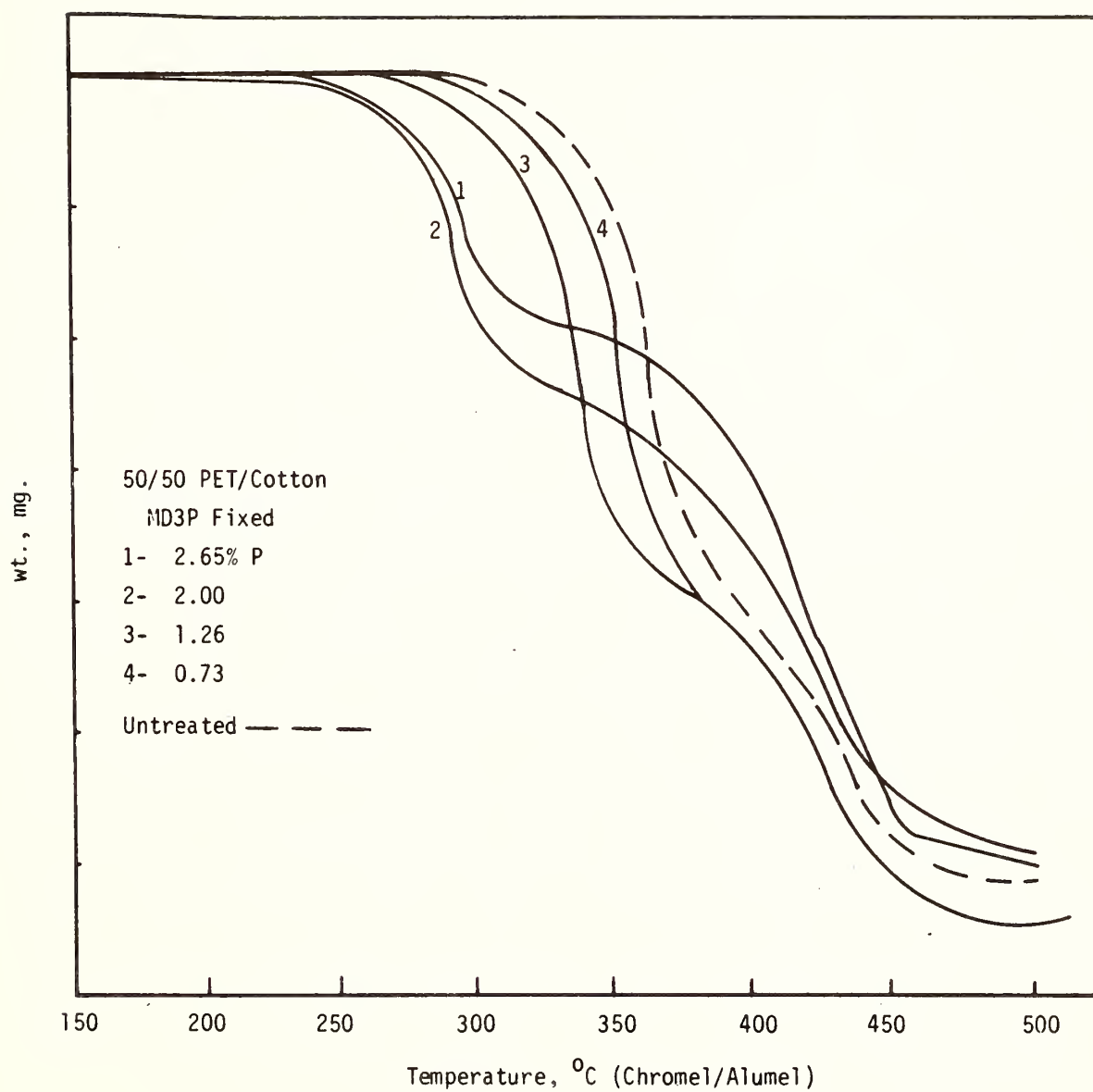


FIGURE 79. TGA of MD3P (fixed) on 50/50 PET/cotton.

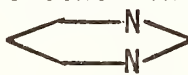
that the efficiency of MD3P as a flame retardant for polyester/cotton blends could probably be enhanced by mixing it with other retardants which have a greater propensity for condensed phase activity. Experiments to combine MD3P with Pyrovatex CP have been inconclusive. Attempts at fixation from baths containing 5-20% MD3P and 10-30% Pyrovatex CP along with Aerotex[®] 23 resin and a phosphoric acid catalyst gave variations in add-on of only 4% on both 50/50 blend and 100% cellulose samples. At the highest add-on levels, the fabric burned readily on the 45⁰ pin frame. Another anomaly of MD3P is the fact that add-ons are achieved that are approximately twice those obtained when other N-methylol propionamide compounds, such as Pyrovatex[®] CP, are applied using the pad-dry-cure technique. To elucidate the nature of the high add-ons of MD3P, 100% cellulose and 50/50 blend fabric with various levels of MD3P were extracted by Soxhlet extraction with methanol. The level of compound remaining in the fabric after extraction was comparable to levels obtained with Pyrovatex[®] CP. Nuclear magnetic resonance spectra of the residue after evaporation of the methanol indicated the majority of the extracted material was 3-diphenylphosphinyl propionamide. As previously noted, the TGA of MD3P, Figure 76, shows a weight loss corresponding to the temperature used in the cure (150⁰C). The precursor to MD3P, which is present after formaldehyde loss, is not water soluble and would not be removed by the afterwash. The Pyrovatex[®] CP precursor is water soluble, and the afterwash leaves only the chemically bound flame retardant. However, these data are consistent with earlier conclusions that fixation reduces volatility to improve condensed phase and vapor phase reactions. Condensed phase reactions decrease the flammable gases to require less phosphorus in the vapor phase. Alternately, efficient vapor phase action decreases the heat return to the fabric to enhance the opportunity of condensed phase reaction, i.e. less volatilization of the flame retardant.

These results indicate that there is some validity to the proposal that a single organophosphorus retardant should be capable of effective action on 50/50 blends, but it will be very difficult to predict a priori the types of structures which will produce the needed balance

a vapor phase and condensed phase activity. However, this work with a single flame retardant substantiates the assumption that condensed and vapor phase retardants work together to give better results on a 50/50 blend than a flame retardant system which displays only one mode of retardance.

3. Other Organophosphorus Retardants

In an attempt to find classes of organophosphorus compounds which might possess the proper balance of volatility and reactivity on 50/50 blends, several structural categories were evaluated. The methyl analog of MD3P, N-methylol-3-(dimethylphosphinyl)propionamide (MDMP) was prepared and studied on 100% cotton and 50/50 polyester/cotton blend fabrics. Using a double pad-dry-cure-rinse process with a bath containing 40% MD3P along with Aerotex[®] 23 and H_3PO_4 , the flame retardant levels were 15% on 100% cotton and 7.5% on a 50/50 blend fabric. These samples were easily ignited and burned completely when subjected to a 45° angle burn test.

Other phosphorus structures prepared and screened included triazaphosphaadamantane; 1,3,2-diazaphosphorinane ; and 2-oxo-2-methoxy-1,3,2-diazaphosphorinane. The triazaphosphaadamantane was obtained from SRRC as a crystalline solid and was applied to both cotton and 50/50 blend fabrics from a chloroform solution. Add-on levels of 2.6% and 2.1%P were achieved on the cotton and the blend respectively. Both fabrics burned readily in the 45° angle pin frame and exhibited OI's of approximately 23.5. Based on these results, work was suspended on this compound.

A more promising series of phosphorus compounds has resulted from studies of cyclotriphosphazene derivatives. Hexakis(2,4,6-tribromophenoxy)cyclotriphosphazene, a previously unknown compound, was prepared in good yield by reaction of the tribromophenoxide with the parent hexachloride. The product was characterized by IR and NMR spectroscopy. It showed good thermal stability with only a small degree of degradation apparent after heating at 250°C for 48 hours. Its 70.5% Br and 4.5% P content should make it an attractive candidate for either topical treatment of fabrics or melt blending during polyester manufacture. Unfortunately, no satisfactory fabric treatment was achieved and thus its potential as a flame retardant remains unmeasured.

As an alternate route to a bromine-containing phosphazene, the attention was focused on the bromoform adduct of hexaallyloxyphospha-

zene previously prepared at SRRC. The hexaallylcyclotriphosphazene was prepared in 80% yield by the reaction of sodium allylate with the tri-chloride. This material was characterized by infra-red, DTA, and NMR. The NMR of the crude reaction mixture shows approximately 95% conversion of the hexachloro compound to the hexaallyloxy. It exists as a thermally unstable, pale yellow oil which resisted attempts at crystallization. An emulsion of the allyl compound was prepared with an almost equal amount of bromoform in conjunction with PVA, sodium bicarbonate and potassium peroxydisulfate and applied to fabric in a one dip, one nip process, dried for 10 minutes at 110° and then cured for 60 minutes at 140°. Oxygen index values were 24.5 for an 11.8% add-on to 65/35 blend fabric, and 25.0 for a 14.0% add-on for 50/50 fabric. In the 45° angle test the samples burned the entire length but showed considerable ignition resistance. At present it is unclear whether these disappointing oxygen index values and flammability characteristics are due to the low weight add-ons used or whether they indicate generally poor efficiency of the retardant.

The picture becomes considerably more promising when the hexaallyloxy phosphazene-bromoform adduct is used in conjunction with THPC. Fabrics of 65/35 blend treated to a 14.9% add-on with this material gave an oxygen index of 25.7, whereas 50/50 blend fabrics treated to a 17% add-on gave an OI value of 27.2. In the 45° angle test, all of the samples showed considerable ignition resistance and the 50/50 blend treated to a 17% add-on failed to burn the entire length. All of the fabrics exhibited a tendency to discolor on heating above 140°C. Because of this and because this system did not appear to offer any significant advantages in terms of flame retardant efficiency, it was not pursued further.

A similar set of experiments was carried out using triallylphosphate in place of the allylphosphazene. Triallylphosphate was allowed to react with bromoform and telomerized in a fashion similar to that used with the phosphazene. The resulting white, stable emulsion was padded onto blend fabrics and evaluated by OI. The adduct appeared to have adequate flame retardant efficiency but the resulting fabrics were stiff

and slightly yellow; thus this system was not examined further.

Other phosphazene systems were also examined. A sample of 6,6-diaminotetrachlorocyclotriphosphazene, a white powder, was isolated from the reaction of a concentrated methylene chloride solution of the hexachlorocyclotriphosphazene and aqueous ammonia. Upon standing, this powder evolved heat and HCl and acquired the characteristics of a highly cross-linking between cyclotriphosphazene residues and is not the same polymer that arises from ammonolysis of the linear polydichlorophosphazene. Such a polymer containing the six membered phosphorus nitrogen ring has not been previously reported.

Several methods of fabric treatment were investigated in attempts to fix aminophosphazene derivatives on to blend fabric. In the first attempt, the hexachloride was padded on to the fabric and then treated with ammonia. These samples were then washed and dried at 100⁰ for three minutes in an attempt to remove untreated starting material which tends to sublime at this temperature. Only low levels of add-on were achieved and are indicative that the reactions to produce a cross-linked polymeric ammonolysis did not take place. Treatment of fabrics with the linear dichlorophosphazene polymer with subsequent reaction with ammonia in organic solvent yielded add-ons of 5% and 10% after washing and drying. Assuming disubstitution by ammonia, this would correspond to approximately 1.6% to 3.2%P on the fabric. These samples exhibited OI values ranging from 25.2 to 27.0. They also exhibited ignition resistance from 5 to 7 seconds with an add-on level of 5.4%. Comparison of these OI values with those obtained using other phosphorus derivatives indicate that the efficiency of the chloro and amino derivatives are nearly twice those of other analogs. This would seem to indicate some promise for these materials as topical flame retardants if complete chlorine removal could be accomplished.

The diaminotetrachloro derivatives have also been evaluated in combination with THPC. A sample of 65/35 polyester/cotton blend fabric treated at a level of 14% add-on exhibited an OI value of 27.7 and these fabrics did not burn on the 45⁰ angle tester. The hand of the fabrics was firm but they were not discolored by heating at 140⁰C for three

minutes. On this basis, this system would seem to have some potential for further development if a satisfactory technique could be developed for its application to fabric.

In order to test the possibility of forming cross-linked methylamine polymers, three aminocyclophosphazenes were treated with an acetone solution of THPC. Tetrachlorodiaminocyclotriphosphazene and THPC gave a crystalline adduct whose melting point and IR spectrum differed from those of the starting materials. Reaction of THPC with hexallylaminocyclotriphosphazene and hexamethylaminocyclotriphosphazene was indicated by the formation of syrupy, viscous products which resisted attempts at purification. Column chromatography of these products gave only a small amount of elutable material indicating formation of telomeric or polymeric products. Samples of 65/35 polyester/cotton were treated with tetrachlorodiaminocyclotriphosphazene/THPC adduct and line dried to give fabrics with approximately 14% add-on. The efficiency of this flame retardant was quite high and the fabrics were not discolored by heating at 140⁰ for three minutes.

4. Mixtures and Precondensates of Phosphorus Retardants

Because it appeared that success in obtaining flame retardant effectiveness with phosphorus systems on blends would require more than simple condensed phase activity by the phosphorus on the cellulosic component, it was decided to more clearly define the limits of this mode of interaction. A series of fabrics was prepared containing various levels of diammonium phosphate as a model non-volatile phosphorus compound at levels of phosphorus ranging from 0.7 to 3.1%. The heat release values for these were then compared with similar fabrics containing both diammonium phosphate and a retardant such as Mobil's Antiblaze[®] 19 which is a potential source of volatile phosphorus. These results are tabulated in Table LII and Figure 80. Heat release values for the diammonium phosphate treated blend show the same general dependency on percent phosphorus as that of phosphoric acid when the values are adjusted to allow for differences in the fabric weight. The blend treated with a mixture of diammonium phosphate and Antiblaze[®] 19 gave a slightly higher heat than that treated with diammonium phosphate alone. However, of perhaps greater significance, the two series of diammonium phosphate/Antiblaze[®] 19 treated blends (one with constant diammonium phosphate content and the other with constant Antiblaze[®] 19 content) fell on the same curve when plotted versus total phosphorus content suggesting that phosphorus from the Antiblaze[®] is essentially as effective as that from the diammonium phosphate in the combined treatment. This is surprising since data obtained on 50/50 blends treated with Antiblaze[®] 19 alone indicated that the latter compound is less effective than diammonium phosphate. This again indicates that the combined action is of a different type rather than either condensed phase or vapor phase active systems alone.

In an attempt to get more data on this type of effect several series of blend fabrics treated with Pyrovatex[®] CP in an unfixed form, resin fixed Pyrovatex[®] 3762 and resin fixed MCC-100[®] were studied by the oxygen bomb technique. The plots of $Y/(1-X)$ versus log percent phosphorus for the Pyrovatex[®] CP and Pyrovatex[®] 3762 are shown in

TABLE LII

ISOPERIBOL RESULTS OF DAP/ANTIBLAZE^(R) 19 TREATED 50/50 POLYESTER/COTTON BLEND

% DAP*	% A-B*	% R	Rate, cal/sec.cm	-ΔH ₁ , cal/gm
<u>Fixed DAP</u>				
4.2 (0.99)	0.9 (0.19)	15.6	59.5 ± 1.9	2205
4.1 (0.96)	2.6 (0.55)	17.0	61.9 2.9	2320
4.0 (0.94)	5.8 (1.22)	18.1	62.2 4.1	2415
3.7 (0.87)	12.6 (2.65)	23.9	52.8 12.8	2239
<u>Fixed Antiblaze^(R)</u>				
0.3 (0.07)	4.8 (1.01)	12.6	65.9 2.4	2436
1.6 (0.38)	4.7 (0.99)	15.6	56.9 1.3	2401
3.1 (0.73)	4.6 (0.97)	18.0	61.3 0.5	2323
4.1 (0.96)	4.6 (0.97)	19.2	55.2 1.8	2213

*Values in parenthesis indicate % phosphorus content.

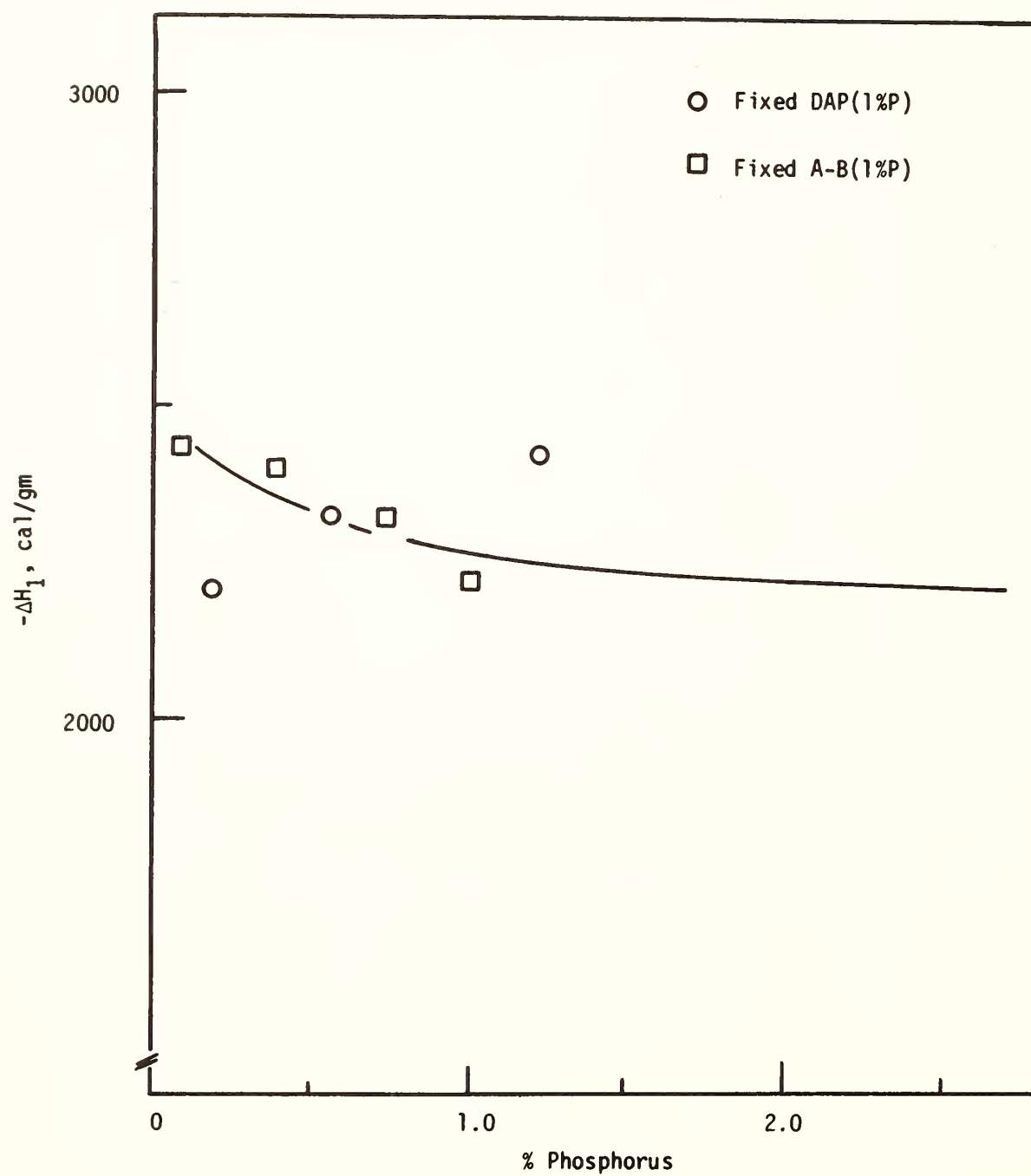


FIGURE 80. Heat release of DAP/Antiblaze[®] treated 50/50 Pet/cotton blend fabrics.

comparison with unfixed Pyrovatex[®] CP on 100% cotton in Figure 81. As expected, the CP treatment was shown to be less effective on the blend than the 100% cellulosic. It is interesting to note, however, that the effectiveness of both treatments is about the same on the blend fabric. Previous results have shown that when the CP is fixed with a melamine resin, its effectiveness decreases markedly on the blend. Experiments have also been carried out in which 65/35 and 50/50 polyester/cotton blends were treated with diammonium phosphate. Two trends in the bomb data were observed. First, it was noted that all of the treatments were shown to be more efficient on the 50/50 blend than on the 65/35. Second, the order of effectiveness for the treatments was diammonium phosphate > CP > 3762 on the same blend fabric. These results can be interpreted as measuring the efficiency of the flame retardant interaction in the condensed phase presumably in the cellulosic part of the blend.

A series of blend fabrics treated with diammonium phosphate has also been examined by oxygen index. Blends of cotton and PET treated with diammonium phosphate showed a strong dependence of oxygen index on the phosphorus content. This is a measure of the effect of the condensed phase interaction with the cellulose component and in agreement with the static oxygen bomb results.

The oxygen bomb calorimetric results from the Monsanto 100/200/300[®] finish on both 65/35 and 50/50 polyester/cotton blend fabrics are given in Table LIII. Also included in Table LIII are the oxygen index and evaluation by the subjective 45° angle burning data for this finish. Since some question has been raised concerning the validity of using the function $Y/(1-X)$ from static oxygen bomb studies on phosphoramidate derivatives such as MC-100[®], the data from these studies were treated in terms of the ratio of ΔH_2 (heat released as measured by static oxygen bomb calorimetry) to the total heat of combustion of the sample $(\Delta H_C^0)_f$. This treatment is shown in Figure 82. These data can be interpreted in the same way as plots of $Y/(1-X)$, and indicate that the high char forming condensed phase efficiency of the treatment on 100% cotton is not duplicated in a blend environment. Subjective evaluation in a 45° angle burning test is consistent with this. These re-

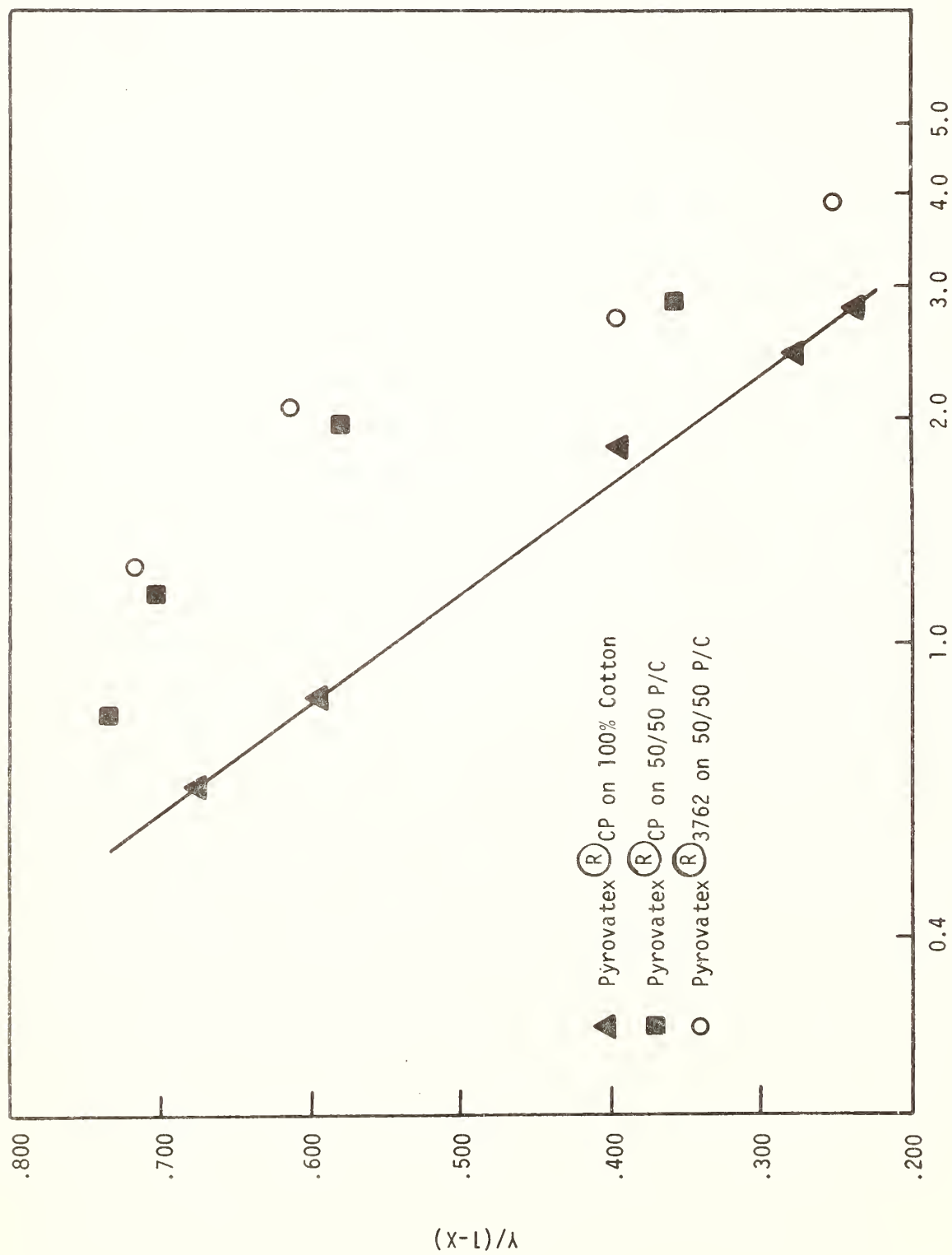


FIGURE 81. $Y/(1-X)$ as a function of $\log \% P$ for Pyrovatex (R) 3762 treated fabrics.

TABLE LIII
FLAMMABILITY OF BLEND FABRICS WITH MCC-100/200/300^(R)

$\%P^{(1)}$	OI	45° Burn	$-\Delta H_2$	$\Delta H_2/(\Delta H_C^0)_F$
1.30 ⁽³⁾	24.8	Difficult to ignite	3595	.74
0.90 ⁽²⁾	23.6	Burns	3799	.77
0.60 ⁽²⁾	22.8	Burns	3852	.78
0.40 ⁽²⁾	22.0	Burns	3929	.79
1.40 ⁽³⁾	26.1	Difficult to ignite	3139	.66
1.00 ⁽³⁾	24.8	Difficult to ignite	3262	.68
0.70 ⁽³⁾	23.6	Burns	3345	.70
0.50 ⁽³⁾	22.5	Burns	3454	.73

¹Estimated on total add-on of finish.

²On 65/35 polyester/cotton blend.

³On 50/50 polyester/cotton blend.

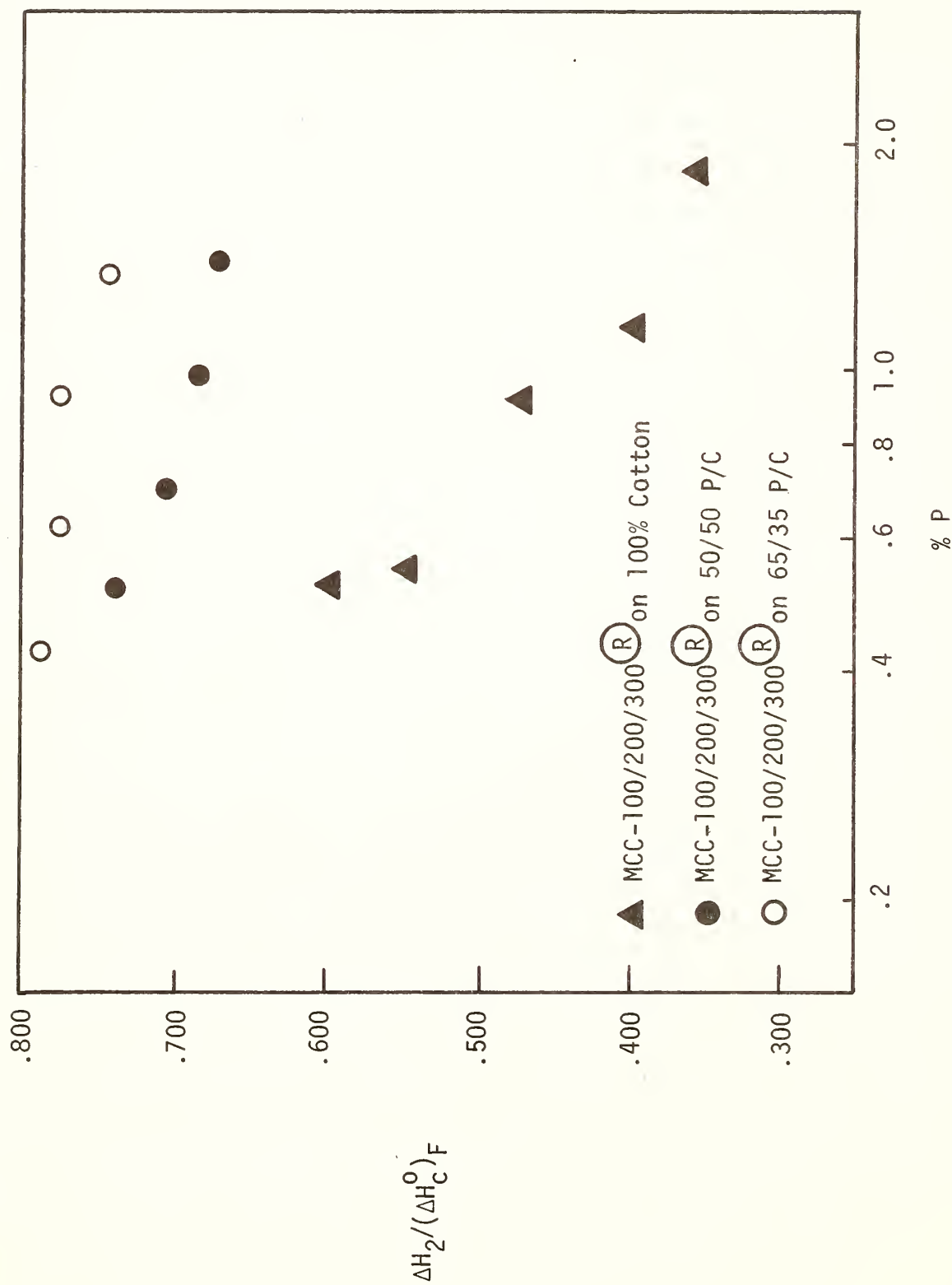


FIGURE 82. $\Delta H_2/(\Delta H_C^0)_F$ as a function of log % P for MCC-100/200/300(R) treated fabrics.

sults are not entirely unexpected since it is quite likely that a large percentage of the retardant is deposited as a coating on the surface of the polyester, and therefore not available for condensed phase interaction with the cellulose. Some evidence in support of this interpretation is found in the change of slope observed in the plot of $\Delta H_2/(\Delta H_C^0)_F$ as one goes from 100% cotton to a 50/50 blend, and from a 50/50 blend to a 65/35 blend. On the other hand, diammonium phosphate, which is probably treated primarily in the cellulose component of the blend with little surface deposition on the polyester, shows no such change of slope as shown in Figure 83. Any phosphorus from the MCC-100^(R) on the surface of the polyester would, of course, be available for other modes of inhibition, but its concentration would probably be too low at these add-ons to be truly effective for flame retardation. Self-extinguishing characteristics were observed for 50/50 blend fabrics over treated with MCC-100/200/300^(R) to add-ons of 35% and phosphorus levels of $\approx 2.5\%$.

These results seemed to confirm previous indications that it should be possible to devise effective flame retardants for polyester/cotton blends based on phosphorus alone. Two fundamental criteria for such flame retardants were defined:

- (1) The FR agent should be relatively active in the condensed phase on the cotton portion of the blend;
- (2) Some significant amount of the phosphorus must volatilize in a suitable temperature range to act as a vapor phase inhibitor for the fuel produced by the decomposing polyester.

These two constraints require that the flame retardant possess an appropriate combination of high thermal stability, low volatility below 300°C and higher volatility above 300°C. Also, since rather large amounts of phosphorus are usually required to pass tests such as that incorporated in FF 3-71, the system should have a phosphorus content approaching 20%.

Although these criteria were later revised, as discussed at the end of this section, they served as effective guides for much of the developmental work during the project. There were several ways of potentially satisfying these requirements, the simplest of which was to

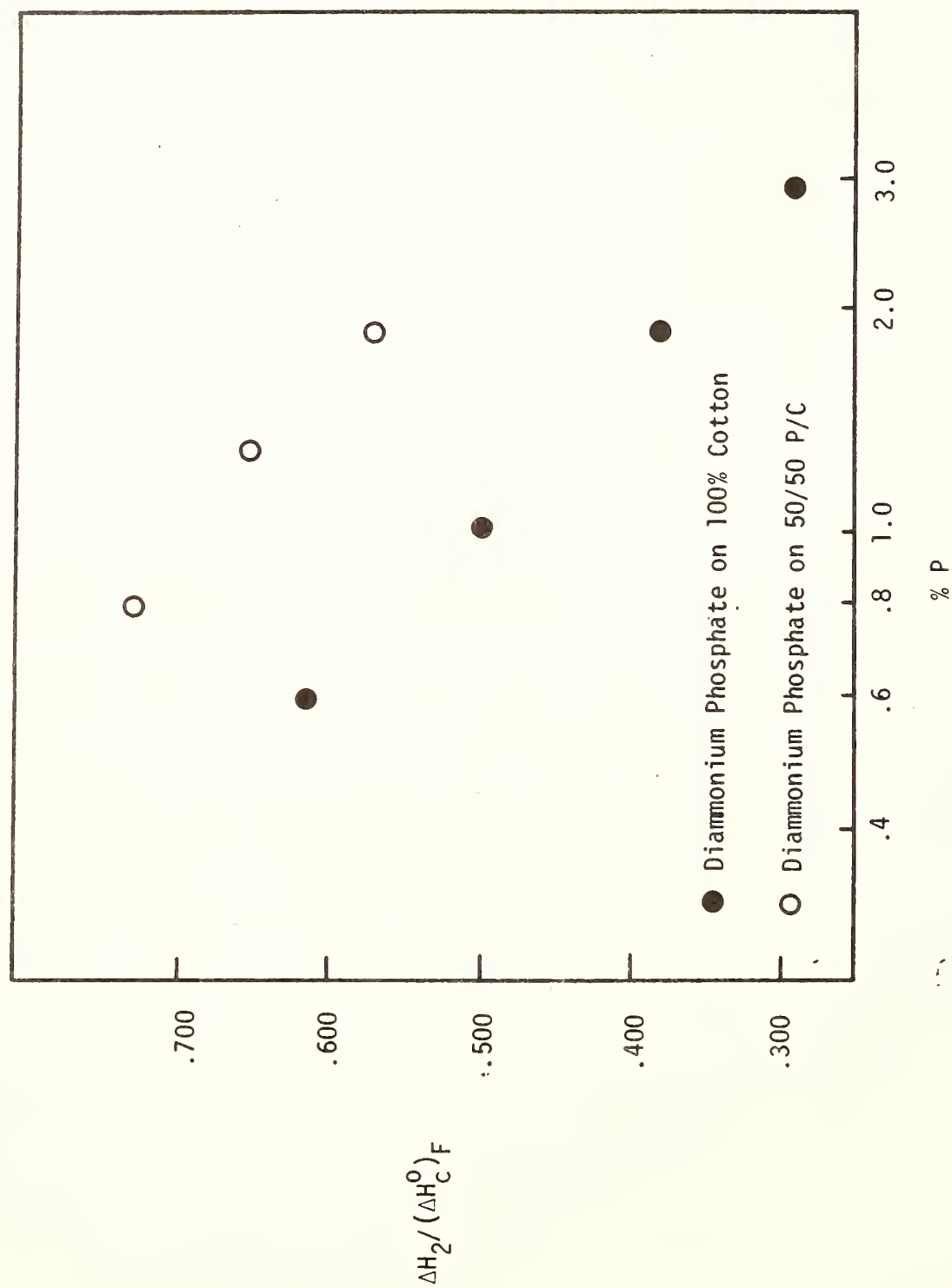


FIGURE 83. Variation of $\Delta H_2 / (\Delta H_C^0)_F$ with phosphorus content of $(NH_4)_2HPO_4$ treated fabrics.

mix known retardants of previously determined activity. Attention was, therefore, focused on mixtures of Pyrovatex[®] CP with THPC/urea, or Pyrovatex[®] 3762 with THPC/urea. The reasoning behind the first formulation was based on the assumption that although THPC/urea acts primarily in the condensed phase in 100% cotton fabric, it could be made to volatilize from a blend where some of the retardant should not be in contact with cellulose. The tendency for volatilization should also be increased by using the THPC in combination with a flame retardant which is inherently more reactive toward the cellulose than is the THPC. Previous research has shown that one flame retardant meeting this requirement was Pyrovatex[®] CP.

A slightly different line of thought was invoked in developing the Pyrovatex[®] 3762/THPC/urea formulation. In this case the system was designed to take advantage of the inherent reactivity of the THPC in the condensed phase while maximizing its tendency for partial volatilization by forming the phosphonium oligomer which should not be capable of penetrating the cellulose and thus should reside on the surface of the fabric. This system would have the advantage of having all of the phosphorus in the same chemical form. Previous work has shown that Pyrovatex[®] 3762 is a more effective retardant for polyester-containing blends than the THPC itself but that it is compatible with these systems. The validity of this approach is demonstrated by the data in Table LIV. These data were particularly encouraging since all of the results were obtained on 50/50 mixtures of the two retardants with no effort toward optimizing the formulations. On the basis of these results it seemed that optimized formulations might be capable of imparting significant flame resistance to cotton/polyester blends at reasonable levels of retardant add-on. In all cases, the fabrics appeared to have fair strength and reasonable, but firm, hand.

As clearly shown by the data in Table LIV, the Pyrovatex[®] 3762/THPC/urea combination is the most effective of the two formulations. This was not unexpected based on previous results with Pyrovatex[®] 3762 alone on blend fabrics. In order to eliminate the problems associated with applying the thermal phosphonium salt precondensate while retain-

TABLE LIV
BURN DATA FROM FABRICS TREATED WITH PHOSPHORUS COMBINATIONS

$x^{(1)}$	45° Burn	FF-3 ⁽²⁾	OI	BOI
<u>THPC/UREA</u>				
.234	DNB ⁽³⁾ (.558) ⁽⁴⁾	2.7	28.8	21.2
.169	I.R. ⁽⁵⁾ (.426)	BEL	27.0	21.0
.124	I.R. (.346)	BEL	24.5	19.5
<u>THPC/Pyrovatex[®]CP/UREA</u>				
.266	DNB (.731)	2.7	28.8	21.5
.206	DNB (.634)	2.9	27.0	21.2
.154	I.R. (.451)	BEL	26.2	21.8
<u>THPC/Pyrovatex[®]3762/UREA</u>				
.216	DNB (.489)	2.9	28.0	22.0
.160	I.R. (.293)	2.7	26.2	20.8
.117	I.R. (.237)	BEL	24.8	19.0

(1) Weight percent of FR finish

(2) Average of three samples, char length in

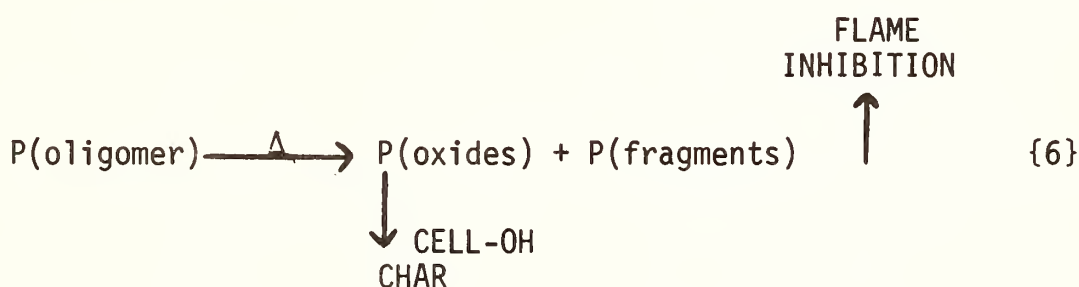
(3) Does not burn

(4) Char weight percent. For samples which DNB charring done with external flame

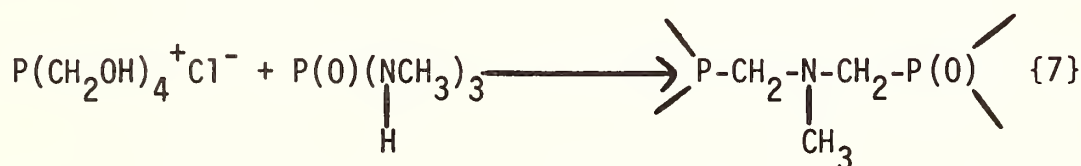
(5) Ignition resistant (>3 seconds with kitchen match)

ing its flame retardant effectiveness, attempts were made to prepare chemical precondensates of tetrakis(hydroxymethyl) phosphonium salts.

Initially it was decided to attempt to synthesize oligomeric structures having two distinct types of linkages between the phosphorus moieties. This decision was based on the assumption that the chemical stability of these bonds would determine the overall efficiency of the oligomer in a degradation scheme such as that shown in reaction {6}.



The simple condensation of MC-100[®] [which had been shown by IR, NMR and mass spectra at the Southern Regional Research Center in 1971 to be primarily $(\text{CH}_3\text{HC})_3\text{PO}$] and an aqueous solution of methylamine with THPC were tried in an attempt to form the oligomeric structures shown in reactions {7} and {8}, respectively.



In the case of the MCC-100, 100 ml. of the 70% aqueous solution of the phosphoramidate was slowly added to 100 ml. of the 85% THPC solution

with stirring. The reaction mixture warmed to $\approx 70^{\circ}\text{C}$ on mixing and was then allowed to cool to room temperature. Under these conditions (initial pH ≈ 2.0 and the presence of free formaldehyde) in addition to the direct reaction between THPC and the phosphoramidate, N-methylolation of the phosphoramidate and the acid catalyzed hydrolysis of the phosphoramidate to H_3PO_4 and methylamine would also occur. The methylamine produced might then react as in reaction {8}.

To form the methylamine precondensate 100 ml. of a 40% aqueous solution of the amine was slowly added with stirring to 100 ml. of the 85% THPC solution.

A third condensation reaction involved neutralization of the 100 ml. of the 80% THPC solution cold with 20% NaOH to a pH ≈ 8.0 . To this was added 100 ml. of the 70% MCC-100^(R) solution and 20 ml. of a 10% MgCl_2 -citric acid catalyst solution. The reaction mixture was heated with stirring to 70°C for 1 hour and then allowed to cool to room temperature.

Although chemical changes in the reaction mixtures had obviously occurred in all three cases ^1H n.m.r., ^{31}P n.m.r. and ^{13}C n.m.r. were used to establish more clearly the nature of these interactions.

The proton n.m.r. of MCC-100^(R) in aqueous solution with DSS as the reference shows $\underline{\text{CH}_3}$, 2.58 ppm, doublet of doublets, $J_{\text{PNCH}} = 12.5\text{Hz}$, $J_{\text{HCHN}} = 5.5\text{Hz}$ and NH, 3.75 ppm, 6-1 line multiplet, $J_{\text{HCHN}} = 5.5\text{Hz}$, $J_{\text{PNH}} = 9.0\text{Hz}$.

When equal volumes of MCC-100^(R) and 80% THPC were mixed as above, the NMR spectrum taken 10 minutes after mixing showed a pair of doublets at 2.55 ppm. and a weaker doublet at 2.85 ppm., $J = 0.5\text{ Hz}$. A very broad doublet was present at 4.3 ppm. When taken at 70°C thirty minutes after mixing, the original - $\underline{\text{CH}_3}$ doublet for MCC-100^(R) at 2.58 ppm. was much weaker while the broadened doublet at 2.8 ppm. increased as did the broad singlet in the 4.1-4.3 ppm. region. The normal doublet for THPC near 4.77 ppm. was replaced by a broad singlet. These spectral changes definitely indicate that reaction has occurred at both phosphorus moieties but do not confirm the direct reaction between the MCC-100^(R) and THPC.

Similar changes showing reaction at both components were observed

in the ^1H spectra for the condensation reactions between THPC and methylamine and THPOH and MCC-100^(R).

In Figures 84 and 85 the ^{31}P n.m.r. of 40% aqueous solutions of THPC and THPC (THPOH) neutralized to a $\text{pH} \approx 8.0$ with NaOH are shown respectively. The ^{31}P n.m.r.'s of the condensation reactions products between THPC- CH_3NH_2 , THPC-MCC-100^(R), and THPOH-MCC-100^(R) are presented in Figures 86 through 88. The chemical shifts relative to phosphoric acid and the integrals for these spectra are tabulated in Table LV.

As expected the THPC spectrum shows a singlet at -26.2 ppm. while THPC neutralized to a $\text{pH} \approx 8.0$ shows the residual THPC signal and the THP (trihydroxymethyl phosphine) multiplet in the region of +23.0 to +31.4 ppm. At this pH THPOH still contains approximately 40% of the phosphonium salt. The THP multiplet arises from the complex equilibrium which exists between the various phosphine moieties present in this solution.

The reaction between THPC and CH_3NH_2 was found to go completely to substituted phosphine derivatives as shown in Figure 86. There is no evidence of any phosphonium salt even though the initial mole ratio of THPC: CH_3NH_2 was approximately 2:1. As in the case of the THPOH spectra the ^{31}P of the precondensate shows the presence of several different phosphine adducts and the mixture is probably an equilibrium between several of them. The chemical shifts of the adduct are all upfield from those of THP alone even though the pH of the solution is similar. This upfield shift is as would be expected for the formation of $\text{P}-\text{CH}_2\text{N}-\text{CH}_2-\text{P}$ bonding. In going from THP (+31.0 ppm.) to $\text{P}\{\text{CH}_2\text{N}(\text{CH}_2\text{CH}_3)_2\}_3$ the chemical shift was found to increase to +65.5.

The ^{31}P n.m.r.'s of the THPC and THPOH oligomers are somewhat more complicated and the interpretations of the chemical shift data less certain. However, tentative assignments can be made on the basis of the results observed above and some related chemical shift data from the literature.

In the case of the THPC-MCC-100^(R) oligomer spectrum (Figure 87) it can be seen that in addition to phosphoric acid formed by the hydrolysis of the phosphoramidate and the residual THPC resonance there are at least

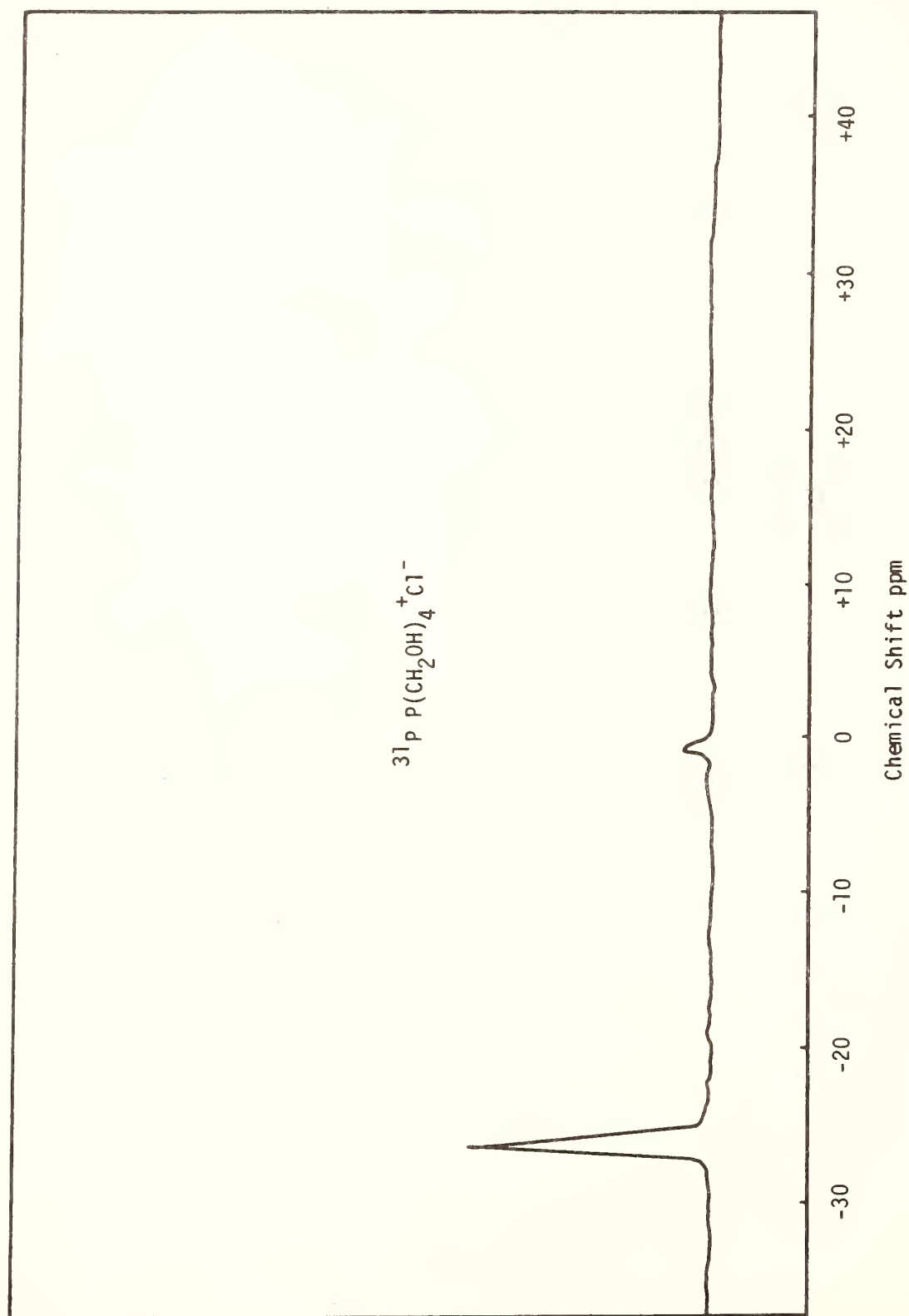


FIGURE 84. ^{31}P spectrum of THPC.

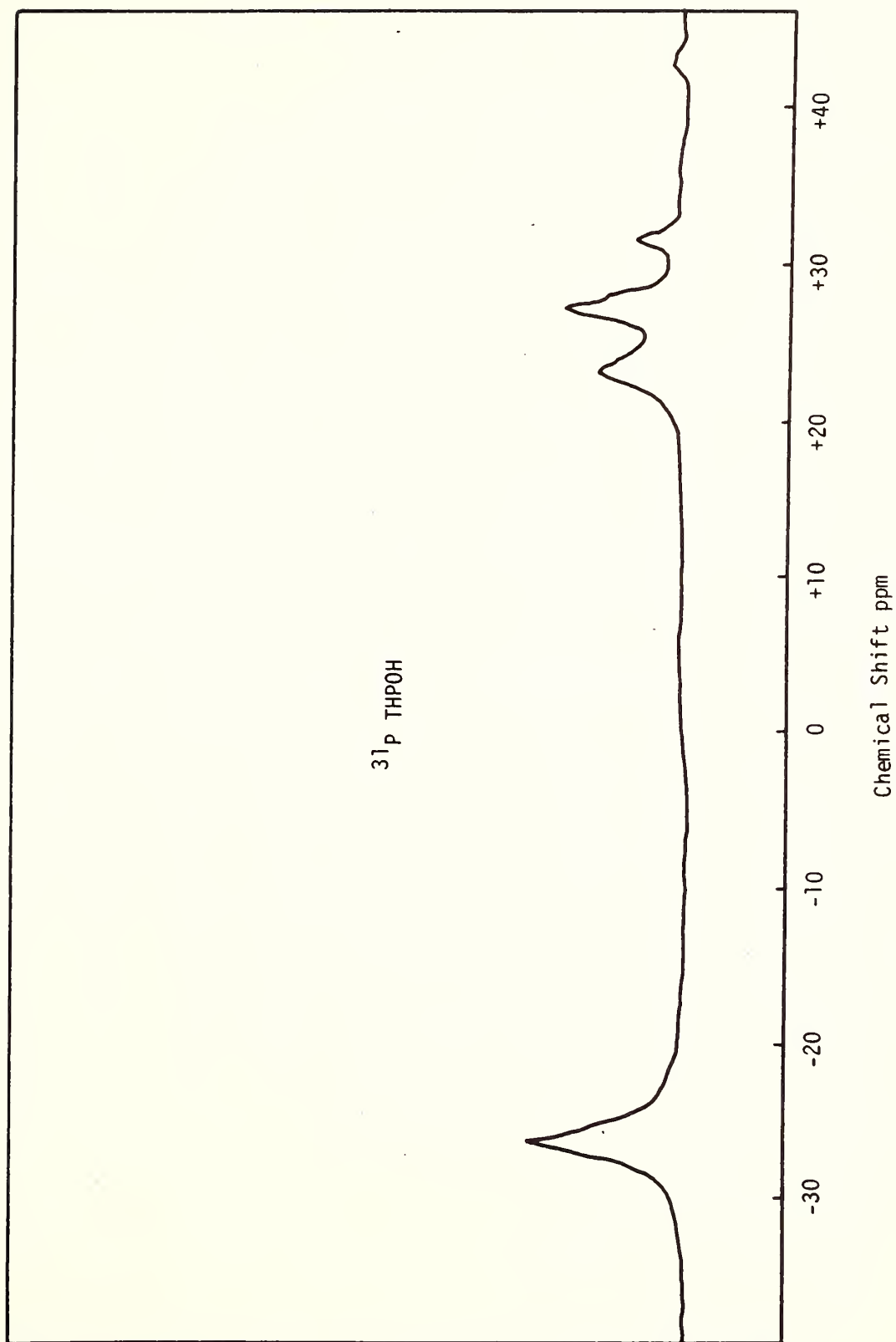


FIGURE 85. ^{31}P spectrum of THPOH.

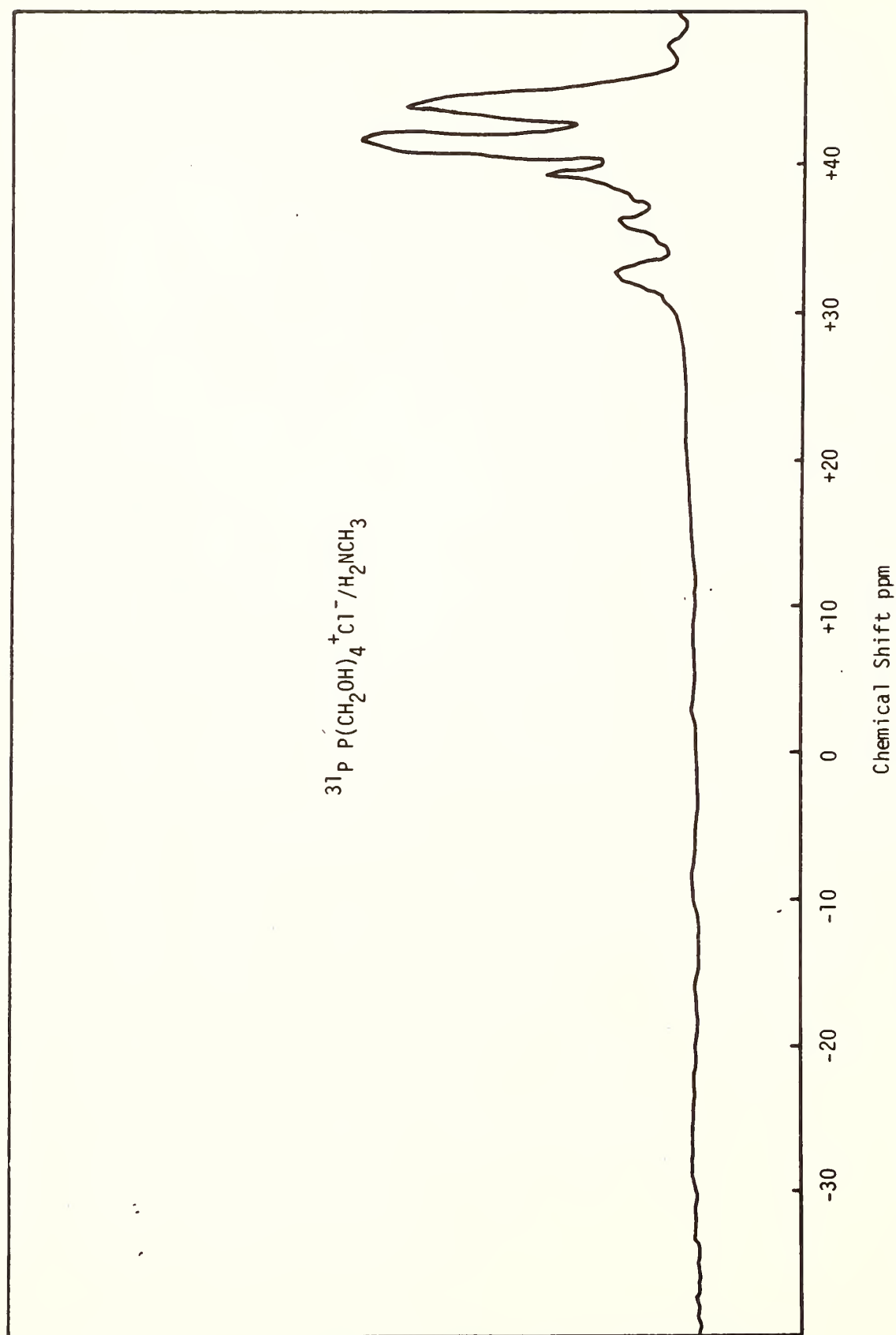


FIGURE 86. ^{31}P spectrum of THPC- CH_3NH_2 oligomer.

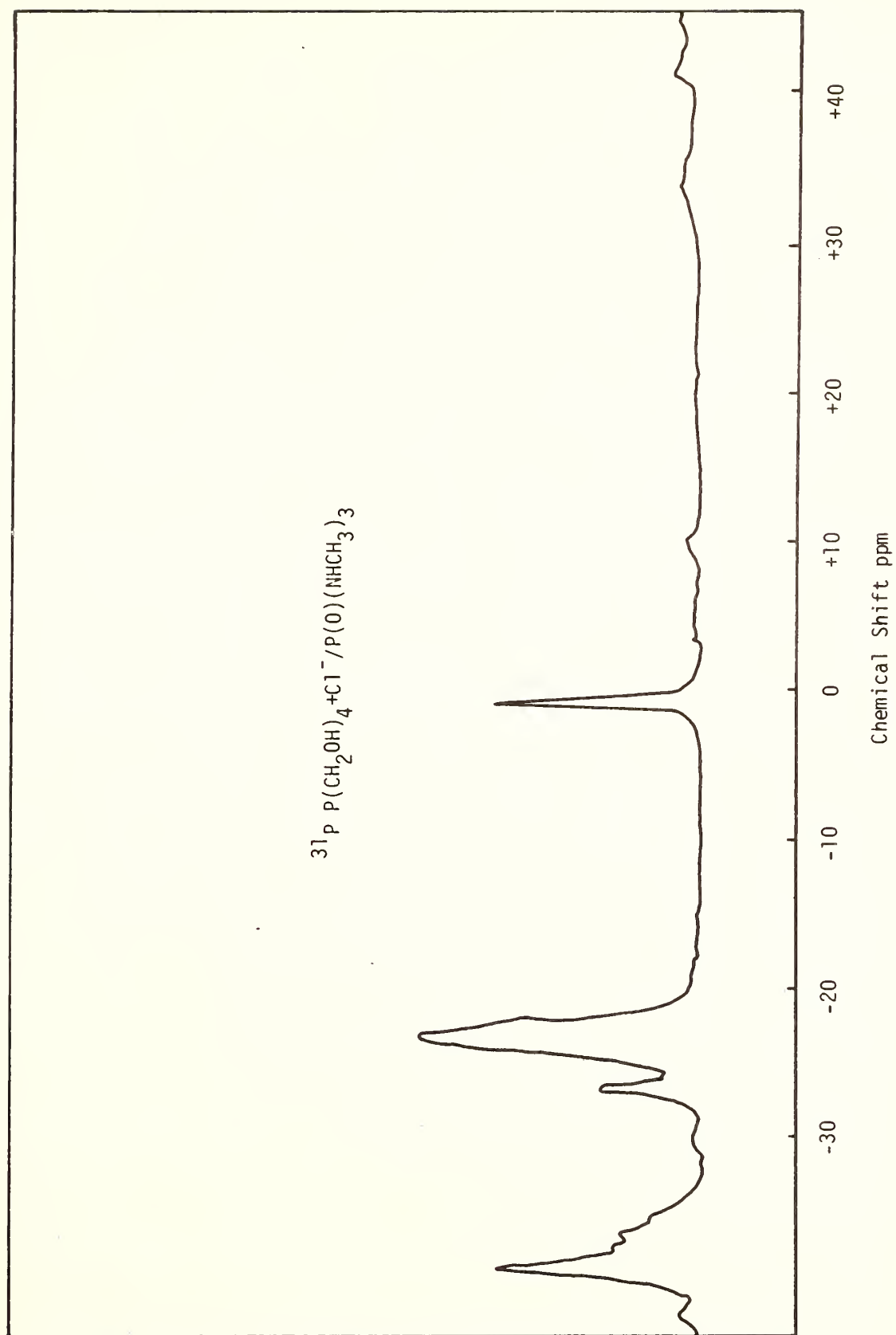


FIGURE 87. ^{31}P spectrum of THPC-MCC 100 R oligomer.



FIGURE 88. ^{31}P spectrum of THPOH-MCC 100 R oligomer.

TABLE LV

³¹P N.M.R. CHEMICAL SHIFTS (1) AND ELECTRONIC INTEGRALS

THPC		THPOH ⁽²⁾		THPC-CH ₃ NH ₂ ⁽³⁾		THPC-MCC-100 ⁽⁴⁾		THPOH-MCC-100 ⁽⁵⁾	
shift, ppm	Area	shift, ppm	Area	shift, ppm	Area	shift, ppm	Area	shift, ppm	Area
-26.1	-----	-26.2	1.46	-26.2	0.00	-42.0	0.06	-38.2(sh)	0.44
		+23.0	0.84	+32.2	0.45	-38.8	0.93	-37.1	0.62
		+27.1	0.88	+36.0	0.34	-35.9(sh)	0.46	-27.2(sh)	0.58
		+31.4	0.30	+39.1	0.65	-26.8	0.30	-23.8	2.72
		>+31.4	0.10	+41.5	1.51	-23.1	2.00	-18.2(sh)	0.08
				+43.8	1.50	00.0	0.42	00.0	0.13
						+31.4>x>50.0	0.64	+33.0	0.37
								+35.2	0.18
								+37.5	0.15
								+41.8(sh)	0.13
								+45.2	0.55

(1) Relative to H₃PO₄, 40 wt % solutions in H₂O.

(2) Ph ≈ 8.0

(3) Mole Ratio THPC-CH₃NH₂ ≈ 2:1.(4) Mole Ratio THPC-MCC-100^(R) ≈ 1:1.(5) Mole Ratio THPC-MCC-100^(R) before neutralization of THPC ≈ 1:1.

3 other types of phosphorus. The phosphorus in the region +30.0 to +50.0 ppm. can be assigned as due to the presence of phosphine phosphorus containing a $\text{P-CH}_2\text{-N}$ bond similar to that formed in the $\text{THPC-CH}_3\text{NH}_2$ oligomer. Although the resonance at -23.1 was originally assigned as unreacted phosphoramidate it now appears that this is due to the substituted phosphoramidate reaction product in the oligomer. This assignment was initially based on the expected insensitivity of the phosphoramidate chemical shift with substitution as shown by the data in Table LVI and also the integrated areas.

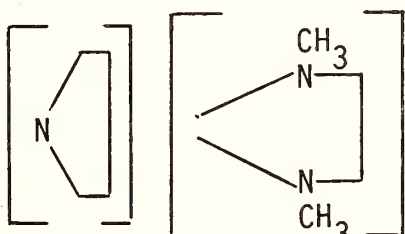
From the integrated areas it can be shown that at least some of the reacted phosphoramidate structure must have chemical shifts similar to MCC-100^(R). Confirmation of reaction at the phosphoramidate nitrogens and this chemical shift assignment was obtained from ^{13}C n.m.r. data provided by Dr. Dan Scharf of Hooker Chemicals and Plastics Corporation. The ^{13}C n.m.r. spectra of a reaction mixture with a 1:3 mole ratio of THPC: MCC-100^(R) showed three types of carbon. At this ratio of THPC: MCC-100^(R) all of the THPC was consumed and the spectra consisted of a broad singlet at 37.6 ppm., a doublet centered at 41.8 ppm. and a sharp singlet at 27.4 ppm. relative to dioxane. The doublet at 41.8 ppm. was assigned to the $\text{P-CH}_2\text{-}$ carbon from the phosphine, the broad singlet to the reacted -N-CH_3 nitrogen methyl carbon and the sharp singlet to the untreated -N-CH_3 nitrogen methyl carbon. These data thus confirm the direct reaction between the THPC and the MCC-100^(R) to form an oligomer with the general structure $\text{P-CH}_2\text{N(CH}_3\text{)P(O)}$ and the assignment of the ^{31}P chemical shift at -23.1.

The remaining resonances in the ^{31}P spectrum are assigned to partially reacted phosphonium derivatives. These downfield shifts are in accord with literature data (72) for substituted THPS^(R) salts and would be expected to be present in this reaction mixture due to the slight excess of available THPC.

The ^{31}P spectrum of the $\text{THPOH-MCC-100}^{(R)}$ oligomer is shown in Figure 88 to be as would be anticipated based on the assignments given for the $\text{THPC-MCC-100}^{(R)}$ oligomer. All of the major spectral shifts can be accounted for by analogy to the previous case. In addition the ratio

TABLE LVI

 ^{31}P Chemical Shifts of Some Selected Phosphoramides⁽¹⁾

<u>Phosphoramide</u>	<u>Chemical Shift, ppm.</u>
$\text{P}(\text{NH}_2)_3$	-22.0
$\text{P}(\text{NHCH}_3)_3$	-24.0
$\text{P}\{\text{N}(\text{CH}_3)_2\}_3$	-23.0
$\text{P}\{\text{N}(\text{CH}_2\text{CH}_3)_2\}_3$	-23.5
OP 	-23.1

⁽¹⁾Reference 72.

of the relative concentration of substituted phosphonium salts to the substituted phosphine is much less than in the case of the THPC-MCC-100^(R) reaction. This reflects the much lower concentration of THPC present due to the neutralization to THPOH. It is also important to note that the less acidic conditions result in much less hydrolysis of the phosphoramidate to phosphoric acid. The ³¹P spectra of these three precondensation reactions are compared to each other in Figure 89 .

With the formation of structurally different THPC precondensates firmly established by n.m.r., calorimetric evaluation of their flame retardant efficiency and mode of action were undertaken. Samples were sent to the University of Maryland for isoperibol calorimetry while the static oxygen bomb calorimetry on the treated fabric and isoperibol chars were performed at Clemson University. The results of these calorimetric investigations are presented in Table LVII through LXIII. The untreated ETIP 50/50 P/C blend was calculated to have a $-\Delta H_2$ heat release of 4064 cal/gm based on a $-(\Delta H_C^0)_F$ of 4690 cal/gm, a $-(\Delta H_C^0)_C$ of 7540 cal/gm and a residue yield of 8.3%.

Unfortunately, the interpretation of the calorimetric data from the phosphorus based non-phosphate or phosphonate FR-systems is not as straight forward as in the case of the halogen or the mixed halogen-model phosphorus compounds presented elsewhere in this report. These difficulties arise because it appears that the systems, as represented by the data in Tables LVII through LXIII, are neither simple cellulose active condensed phase nor classical vapor phase retardants. Their mode of inhibition seems to involve a complex interaction in the condensed phase with both the cellulose and polyester. In addition, it may also involve as yet an undefined vapor phase activity. Another difficulty involved in interpreting this data is that no classical vapor phase only, phosphorus compounds were found during the course of this study. Thus, no model compound data on this type of flame inhibition for phosphorus is available. Because of these considerations any discussions of these data must, at the present time, be limited to mechanistic generalizations and comparisons of their relative efficiencies.

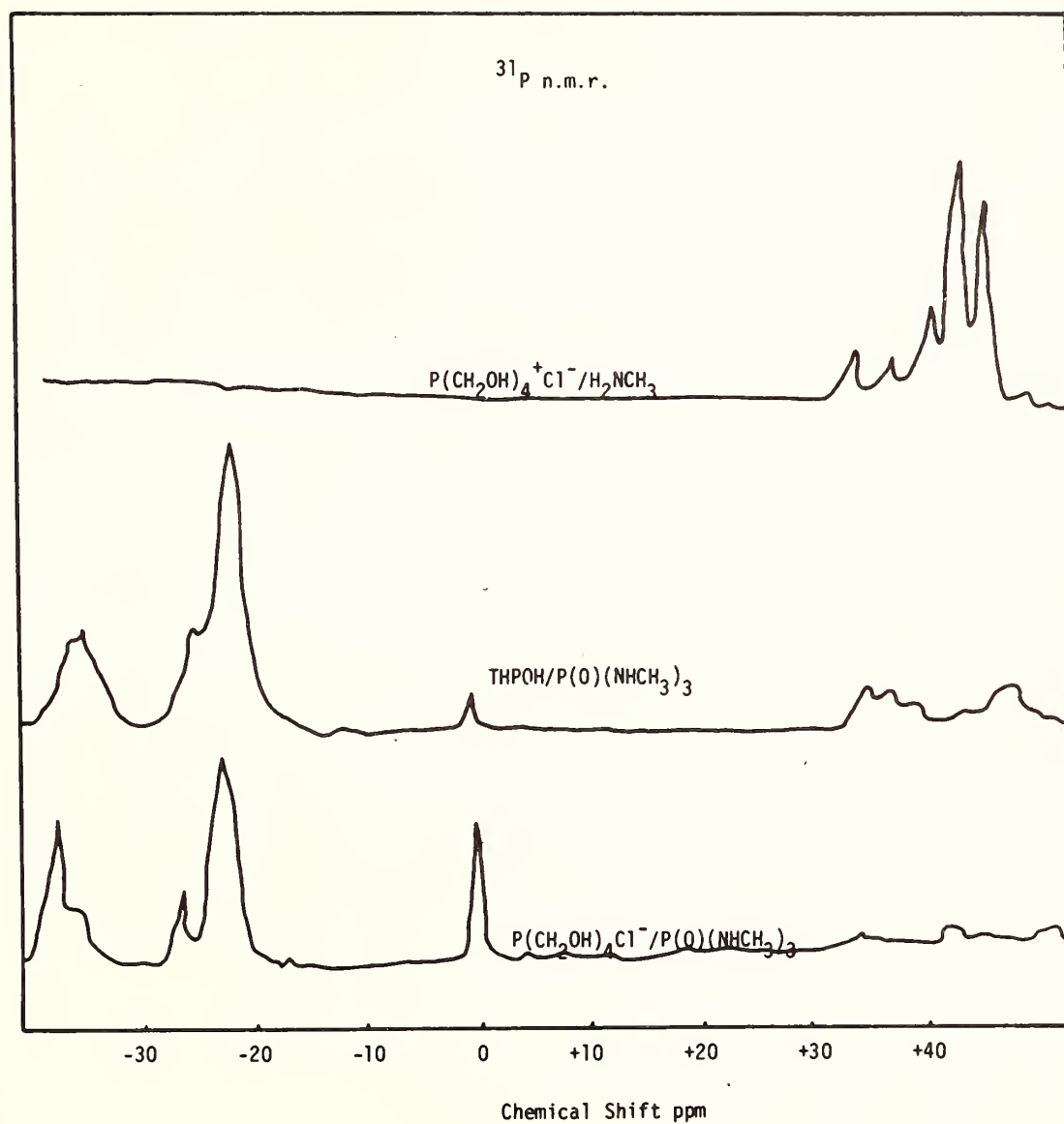


FIGURE 89. Comparison of ^{31}P spectra of phosphonium salt oligomers.

TABLE LVII
CALORIMETRIC RESULTS FROM EIP 50/50 BLEND FABRIC TREATED WITH THPC/UREA (i) AND $(\text{NH}_4)_2\text{HPO}_4$

% Finish	% P	% R	Rate, cal/cm-sec	$-\Delta H_1$, cal/gm	$-(\Delta H_C^0)_F$, cal/gm	$-(\Delta H_C^0)_R$, cal/gm	$-\Delta H_2$, cal/gm
THPC/Urea							
6.9	0.9	19.6	60.5 ± 5.6	2173	4645	6282	3444
8.7	1.2	20.9	64.7 ± 3.8	1967	4623	6142	3339
12.8	1.9	24.7	58.2 ± 3.5	1774	4600	6020	3113
16.8	2.4	27.4	59.6 ± 3.8	1661	4558	5903	2940
21.4	3.3	30.2	60.5 ± 2.7	1558	4545	5688	2827
$(\text{NH}_4)_2\text{HPO}_4$							
3.1	0.72	14.1	60.3	2419	4495	6407	3592
4.8	1.12	15.0	60.6	2391	4489	6217	3556
6.5	1.52	17.3	61.1	2318	4427	6000	3348
9.8	2.31	19.5	54.5	2077	4386	5718	3271
11.1	2.60	20.5	48.6	2021	4280	5593	3133
13.4	3.15	25.0	52.7	1868	4225	5315	2896

(1) Applied by a pad/dry/cure using a formulation suggested by Mr. George Drake of the Southern Regional Research Center.

TABLE LVIII

Calorimetric Results From the ETIP 50/50 Blend Fabric Treated With Pyrovatex ⁽¹⁾R 3762

% Finish	% P	% R	Rate, cal/sec-cm	$-\Delta H_1$, cal/gm	$-(\Delta H_C^0)_F$, cal/gm	$-(\Delta H_C^0)_R$, cal/gm	$-\Delta H_2$, cal/gm
50/50 P/C							
7.9	1.24	18.0	55.9 \pm 0.8	2033	4661	6194	3546
12.5	2.05	25.2	55.7 \pm 4.3	1846	4656	5980	3149
17.0	2.70	26.4	55.2 \pm 5.2	1823	4661	5863	3113
24.1	3.90			DID NOT BURN			
65/35 P/C							
7.1	1.12	15.1	51.4 \pm 0.7	2097	4858	6294	3908
11.2	1.87	19.4	53.1 \pm 2.2	1937	4866	6444	3616
15.0	2.31	23.2	54.1 \pm 2.9	1779	4887	6191	3451
21.1	3.72	28.7	62.0 \pm 6.5	1742	4908	5710	3269

⁽¹⁾Applied by a pad/dry/cure using the formulation suggested by Ciba-Geigy.

TABLE LIX

Calorimetric Results From the ETIP 50/50 Blend Fabric Treated with Combination Flame Retardants

		THPC and Pyrovatex ^(R) CP, THPC and Pyrovatex ^(R) 3762				
% Finish	% P	% R	Rate, cal/sec-cm	$-\Delta H_1$, cal/gm	$-(\Delta H_C^0)_F$, cal/gm	$-(\Delta H_C^0)_R$, cal/gm
THPC and Pyrovatex ^(R) CP/Urea ⁽¹⁾						
7.5	1.0	18.4	62.2 ± 1.0	2183	4632	6169
8.8	1.2	19.4	62.9 ± 12.3	2143	4661	6153
11.2	1.6	21.5	66.2 ± 1.8	1998	4671	5962
15.4	2.5	26.6	55.3 ± 3.2	1692	4526	5782
21.6	3.5			DID NOT BURN		
Pyrovatex CP, THPC/Urea ⁽²⁾						
8.0	1.2	19.9	61.3 ± 5.1	2194	4614	6017
13.3	2.0	23.2	58.6 ± 4.3	1928	4595	5932
15.4	2.3	24.7	60.8 ± 3.0	1844	4778	5835
18.6	2.9	26.6	62.1 ± 4.0	1744	4560	5642
THPC and Pyrovatex ^(R) 3762/Urea ⁽³⁾						
11.4	~1.71 ⁽⁴⁾	24.5	58.8 ± 5.0	1724	4655	5960
14.0	~2.10	27.9	56.6 ± 0.8	1574	4538	5988
23.0	~3.50			DID NOT BURN		

(1) Pad bath contained a 1:1 mole ratio of THPC to Pyrovatex ^(R)CP.(2) Fabric treated to 1.18% P as Pyrovatex ^(R)CP and was then topped with THPC/Urea.(3) Pad bath contained a 1:1 solids of THPC to Pyrovatex ^(R)3762.

TABLE IX

Calorimetric Results From the ETIP 50/50 Blend Fabric Treated With THPC-MCC-100^(R) Oligomer ⁽¹⁾

% Finish	% P	% R	Rate, cal/sec-cm	$-\Delta H_1$, cal/gm	$-(\Delta H_C^0)_F$, cal/gm	$-(\Delta H_C^0)_R$, cal/gm	$-\Delta H_2$, cal/gm
THPC-MCC-100 ^(R) Oligomer/Urea ⁽²⁾							
6.6	1.3	20.6	59.5 \pm 5.0	2198	4685	6159	3416
9.6	1.8	22.3	60.0 \pm 2.3	2131	4627	5728	3350
13.6	2.5	25.9	61.2 \pm 5.0	2002	4610	5800	3108
18.2	3.5	31.6	55.5 \pm 8.0	1809	4572	5449	2850
24.5	4.6	35.6	65.5 \pm 2.7	1650	4479	4839	2749
THPC-MCC-100 ^(R) Oligomer/MCC-200 ^(R) ⁽³⁾							
9.0	1.7	21.3		1911	4752	6081	3457
14.0	2.8	26.5		1842	4747	5786	3214
21.0	3.7	28.5		1778	4727	5733	3093

⁽¹⁾ Mole Ratio of THPC: MCC-100^(R) in precondensation reaction 1:1.⁽²⁾ Applied by a pad/dry/cure with urea.⁽³⁾ Pilot plant run at Southern Regional Research Laboratory using MCC-200^(R) and MCC-300^(R) as the resin and catalyst respectively.

TABLE LXI

Calorimetric Results From the ETIP 50/50 Blend Fabric Treated with THPOH-MCC-100 ^(R) oligomer (1)							
% Finish	% P	% R	Rate, cal/sec-cm	$-\Delta H_1$, cal/gm	$-(\Delta H_C^0)_F$, cal/gm	$-(\Delta H_C^0)_R$, cal/gm	$-\Delta H_2$, cal/gm
THPOH-MCC-100 ^(R) oligomer/MCC-200 ^(R) (2)							
11.2	1.1	22.3	64.7	1801	4745	6324	3335
14.9	1.6	23.4	63.3	1746	4736	6305	3260
18.4	2.1	27.2	62.0	1658	4722	6030	3082
21.6 ⁽³⁾	2.4	29.0	69.3	1599 \pm 74	4714	5897	3004
THPOH-MCC-100 ^(R) oligomer/THPC/MCC-200 ^(R) (4)							
12.1	1.7	23.1	65.2	1725	4747	6290	3294
15.6	2.2	27.0	72.4	1604	4744	6079	3103
19.0	2.8	29.6	70.0	1523	4702	5906	2954
22.7 ⁽³⁾	3.3	30.5	71.2	1528 \pm 118	4704	5580	3002

(1) Mole Ratio of THPC: MCC-100^(R) in precondensation reaction 1:1 before neutralization of THPC to THPOH

(2) Applied by a pad/dry/cure with MCC-200^(R)

(3) Ignition resistant

(4) Solids ratio of added THPC: THPOH-MCC-100^(R) oligomer 1:1. Applied by a pad/dry/cure with MCC-200^(R)

TABLE LXII

Calorimetric Results From the ETIP 50/50 Blend Fabric Treated with THPC-CH₃NH₂ Oligomer (1)

% Finish	% P	% R	Rate, cal/sec-cm	$-\Delta H_1$, cal/gm	$-(\Delta H_C^0)_F$, cal/gm	$-(\Delta H_C^0)_R$, cal/gm	$-\Delta H_2$, cal/gm
THPC-CH ₃ NH ₂ oligomer/MCC-200 (R) (2)							
6.6	0.7	17.3	63.6	2040	4753	6666	3600
8.2	0.9	17.6	65.0	1938	4750	6642	3581
10.8	1.2	21.0	66.1	1729	4707	6585	3324
13.8	1.5	22.4	61.8	1758 ± 127	4713	6046	3359
THPC-CH ₃ NH ₂ oligomer/THPC/MCC-200 (R) (3)							
9.7	1.5	22.1	69.4	1852	4741	6167	3378
12.2	1.6	23.7	65.1	1848	4727	5990	3307
16.5	2.9	26.0	67.9	1727	4695	5957	3146
19.5	3.0	27.5	65.7	1575	4670	5857	3059
23.5 ⁽⁴⁾	3.7	29.9	64.9	1430	4609	5651	2919

(1) Mole ratio of THPC: CH₃NH₂ in precondensation reaction 1:1.

(2) Applied by a pad/dry/cure with MCC-200 (R).

(3) Solids ratio of THPC: THPC-CH₃NH₂ oligomer 3:1. Applied by a pad/dry/cure with MCC-200 (R).

(4) Ignition resistant.

TABLE LXIII
Calorimetric Results From DuPont 50/50 P/C and 50/50 900F[®]/Cotton Blend Fabrics
with the THPC-CH₃NH₂ Oligomer

% Finish	% P	% R	Rate, cal/sec-cm	-ΔH ₁ , cal/gm	-(ΔH _C ⁰) _F , cal/gm	-(ΔH _C ⁰) _R , cal/gm	-ΔH ₂ , cal/gm
THPC-CH ₃ NH ₂ oligomer/MCC-200 [®] /DuPont 50/50 P/C							
control	0.0	1.5	70.0	2845			
7.2	0.6	17.4	66.4	2014	4713	6837	3523
8.7	0.8	19.1	62.2	1879 ± 139	4692	6684	3415
12.0	1.1	21.8	65.0	1754 ± 74	4701	6542	3275
15.1	1.3	23.0	63.3	1769	4617	6594	3100
THPC-CH ₃ NH ₂ oligomer/MCC-200 [®] /DuPont 900F [®] 50/50 P/C							
control	0.0	4.6	43.7	2809			
7.7	0.8	18.8	58.8	1788	4686	6447	3474
10.0	1.2	21.8	59.4	1688	4654	6421	3254
12.7	1.5	23.5	57.2	1783	4658	6418	3150
16.3 ⁽¹⁾	1.7	28.0	52.6	1606 ± 117	4655	6369	2872

(1) Ignition resistant.

If ΔH_1 for all of the data in Tables LVII through LXIII were plotted versus the % P in the finish, with the possible exception of three treatments, all of the data points would fall within the boundaries of the generalized response curve given in Figure 90. However when the data are plotted vs $\Delta H_1/(\Delta H_C^0)_F$, the distinction between these finishes becomes less pronounced (Figure 91). The three finishes which may be exceptions to this behavior are $(\text{NH}_4)_2\text{HPO}_4$ and the two THPC-MCC-100^(R) oligomer finishes given in Table LXI.

Two other generalized response curves for these finishes may be constructed from these data and are presented in Figures 92 and 93. In Figure 92 ΔH_2 is plotted as a function of % P and no exceptions to this response are observed for any of the data. In Figure 93, R is plotted as a function of the % P in the finish and in this case the $(\text{NH}_4)_2\text{HPO}_4$ data once again appears to deviate from the response observed for the other systems.

The deviation of the $(\text{NH}_4)_2\text{HPO}_4$ data in Figures 90 and 93 might be rationalized in terms of its activity in the condensed phase of cellulose. Since it can only interact with the cellulose substrate and is nonvolatile it would be expected to be the least efficient treatment in reducing ΔH_1 from a blend. On the other hand, it should be the most efficient in terms of residue formation, especially at low P add-ons. However, this is not found to be the case. Even at only 1% P it is a significantly less efficient char former than the other treatments. This is not due to some of the $(\text{NH}_4)_2\text{HPO}_4$ depositing on the surface of the polyester and hence not available to interact with the cellulose substrate. If this were the situation, then the oligomeric finishes should be even less efficient char formers since they are likely to have even a larger percentage of their phosphorus is on the surface of the polyester. There is the possibility that some of the other finishes increase the residue forming tendencies of the polyester but this cannot be ascertained with any certainty from the data. This would explain the decreased efficiency of $(\text{NH}_4)_2\text{HPO}_4$ which is the same as the other finishes as shown in Figure 93. In line with this conclusion it can be seen by a careful comparison of the data in Tables LVII through

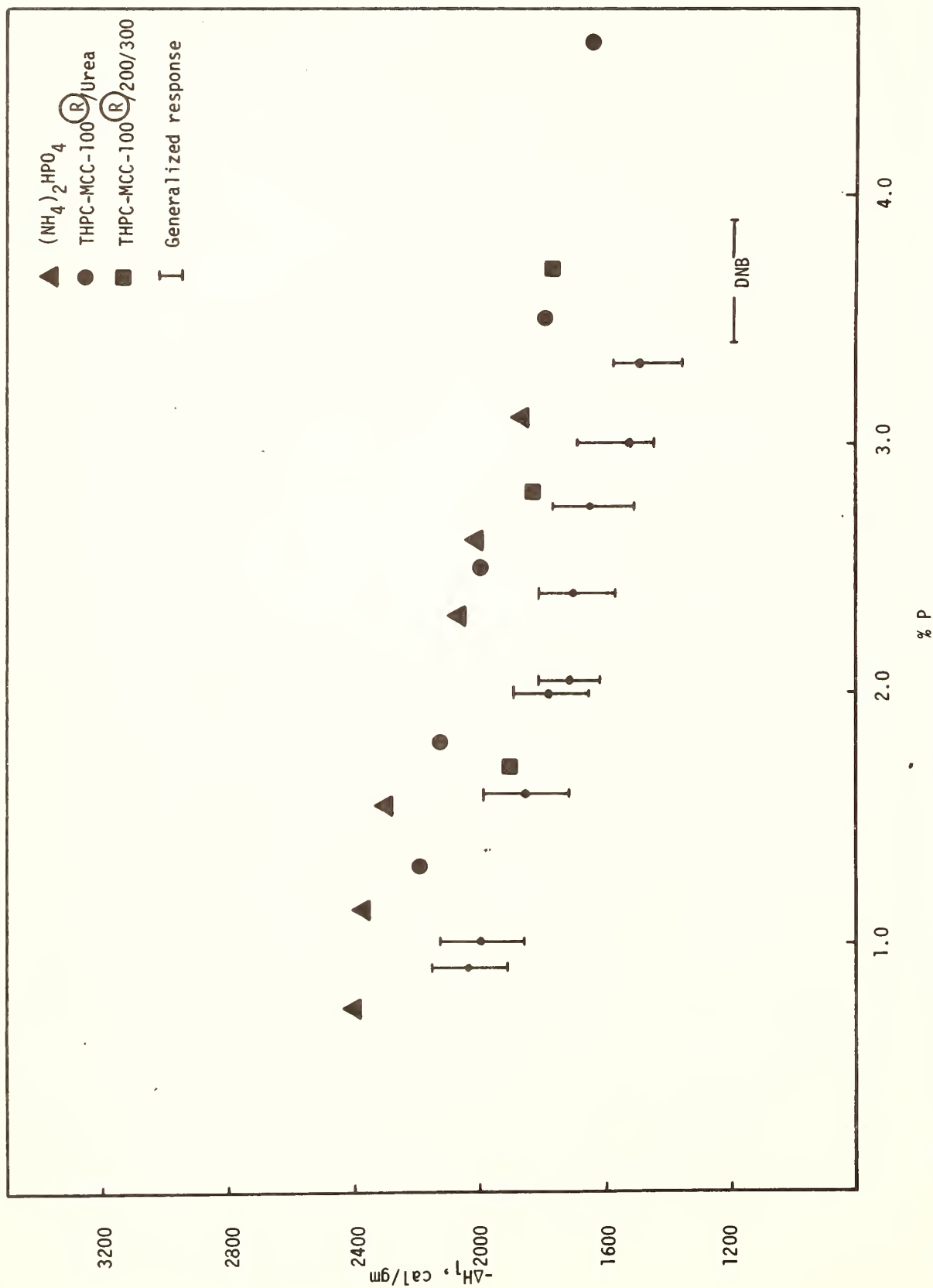


FIGURE 90. Generalized relation between ΔH_f and %P for flame retardant 50/50 PET/cotton blends.

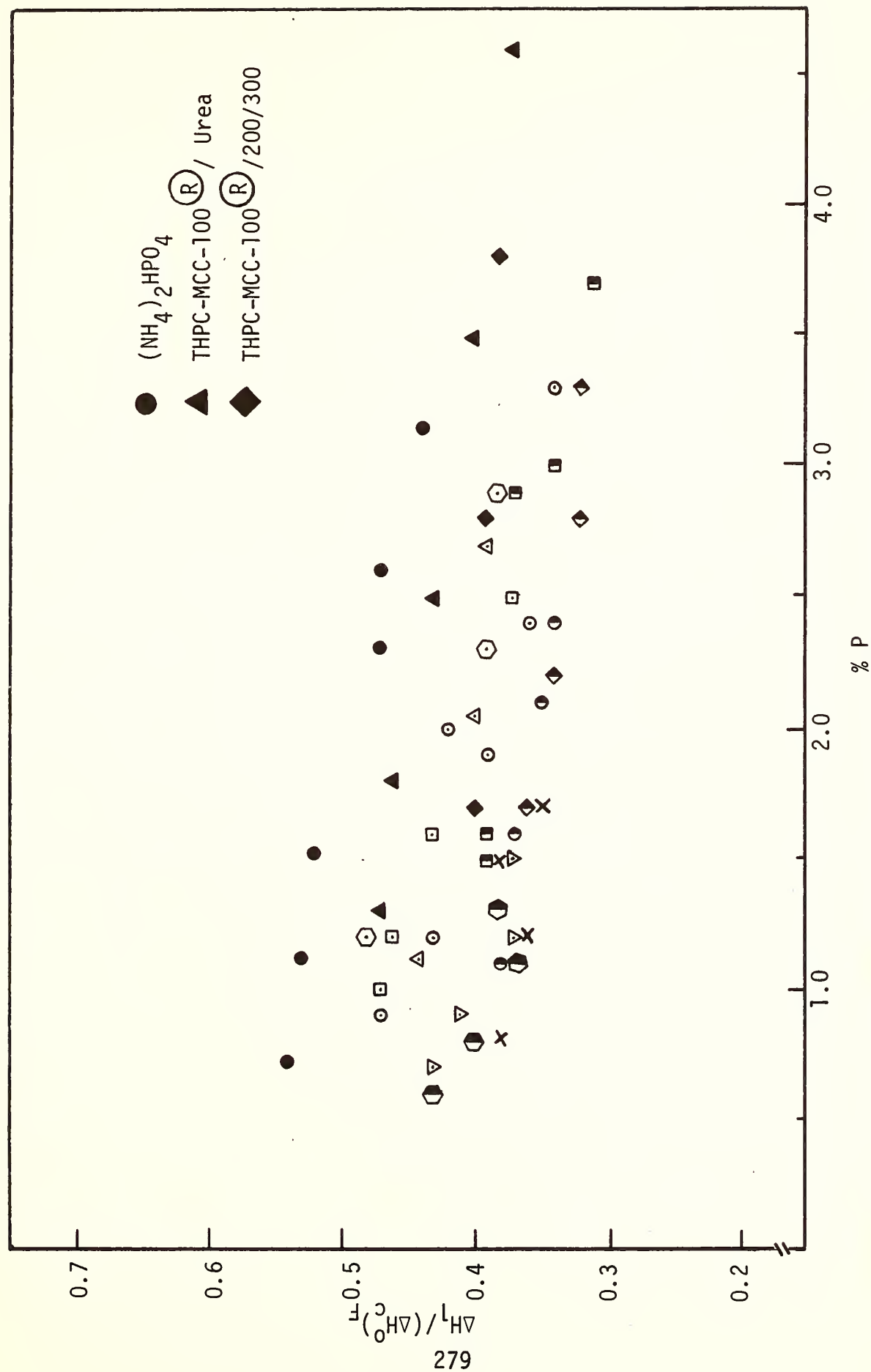


FIGURE 91. $\Delta H_T / (\Delta H_C^0)_F$ as a function of %P for flame retardant 50/50 PET/cotton blends.

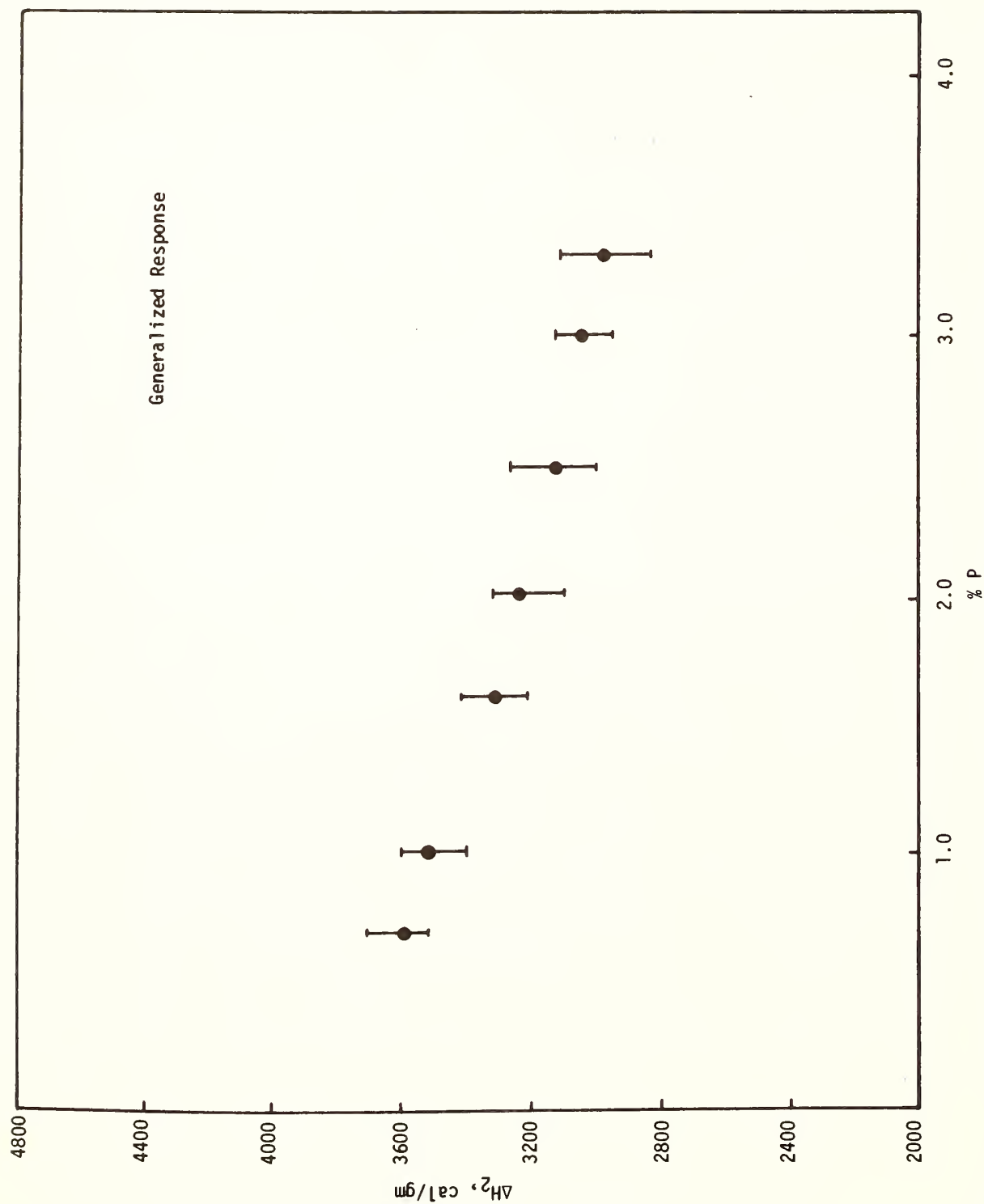


FIGURE 92. Generalized function of ΔH_2 vs. %P for flame retardant 50/50 PET/cotton blends.

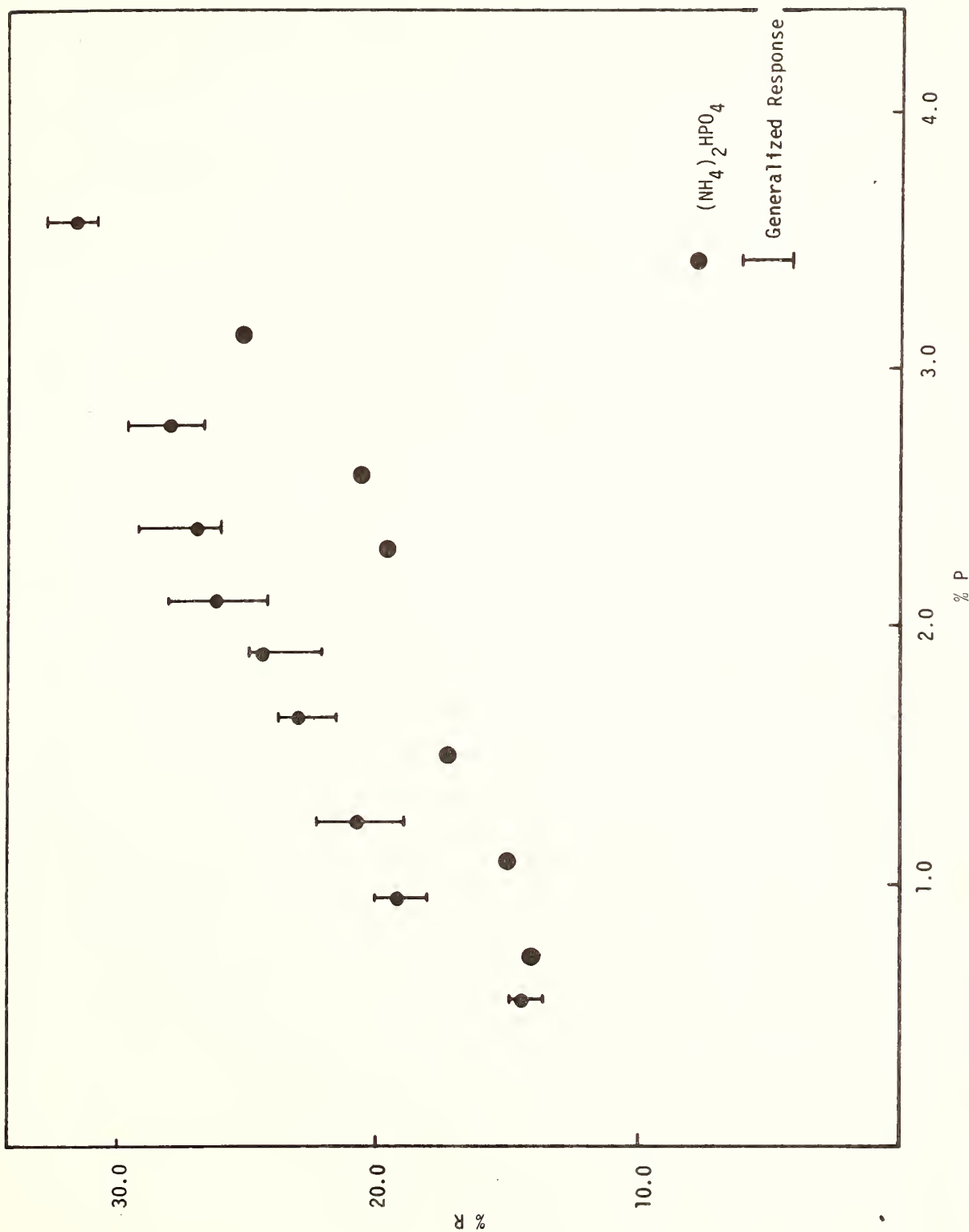


FIGURE 93. Generalized dependence of residue yield on initial P content of FR 50/50 PET/cotton blends

LXIII with the generalized response curves in Figures 90 and 92 that those finishes whose ΔH_f data tends to lower than the average also tend to yield above average residues.

That these finishes, with the previously discussed exceptions noted, behave similarly is not too surprising when their chemical similarity is noted. They all have in common the OP $(CH_2R)_3$ structure to varying degrees and might be expected to behave similarly on the same substrate when compared on the basis of their % P.

Although a positive mechanistic statement cannot be made at this time this data provided a valuable insight into the approach necessary to obtain the maximum flame retardant effectiveness. Since their mode of action is apparently similar, and since there appears to be little difference in efficiency in terms of the oligomers structure, it was concluded on the basis of these results, that maximizing the phosphorus content would lead to corresponding increases in FR effectiveness.

The results presented in Table LXIV and plotted in Figure 94 for the three different blend fabrics treated with the THPC- CH_3NH_2 oligomer give still another indication of the complex nature of the interaction between these phosphorus structures and the blend substrate. In sharp contrast to the data for the H_3PO_4 treated Dacron^(R) and 900F^(R) 50/50 blends, the ΔH_f data for the THPC- CH_3NH_2 finished blends appears to be independent of the bromine content of the 900F^(R). Unfortunately, fabrics were not treated with higher phosphorus contents to confirm the absolute shape of the ΔH_f response curve. The two highest add-on's from the 900F^(R) containing blend series were observed to be significantly more ignition resistant than the corresponding add-ons for the Dacron^(R) blend. This indicates that the shape of the response curve is in fact similar to that found with the H_3PO_4 /900F^(R) series and shown by the dashed line in Figure 94 .

In general, all of the oligomers studied so far exhibit a high degree of stability once formed and may be stored for several weeks without any appreciable changes in chemical or physical properties occurring. The product obtained in the oligomerization reaction is also dependent on the ratio of retardants employed, although the

TABLE LXIV
 CALORIMETRIC RESULTS FROM THE ETIP 50/50 BLEND FABRIC TREATED WITH
 A THPS[®]/MCC-100[®]/UREA PRECONDENSATE⁽¹⁾
 COMPARED TO THPC/UREA

% Finish	% P	% R	ΔH_f
Oligomer			
8.9	1.46	19.1 \pm 0.3	1936 \pm 36
12.3	1.95	20.3 \pm 0.3	1847 \pm 116
16.7	2.40	25.4 \pm 0.3	1826 \pm 28
23.4	3.60	27.9 \pm 0.7	1648 \pm 59
THPC/Urea			
6.7	0.82	17.1	2008
12.4	1.90	22.3	1868
21.5	3.30	31.7	1745

(1) Solids ratio of THPS[®]. MCC-100[®] in the
 precondensation reaction \cong 5:1.

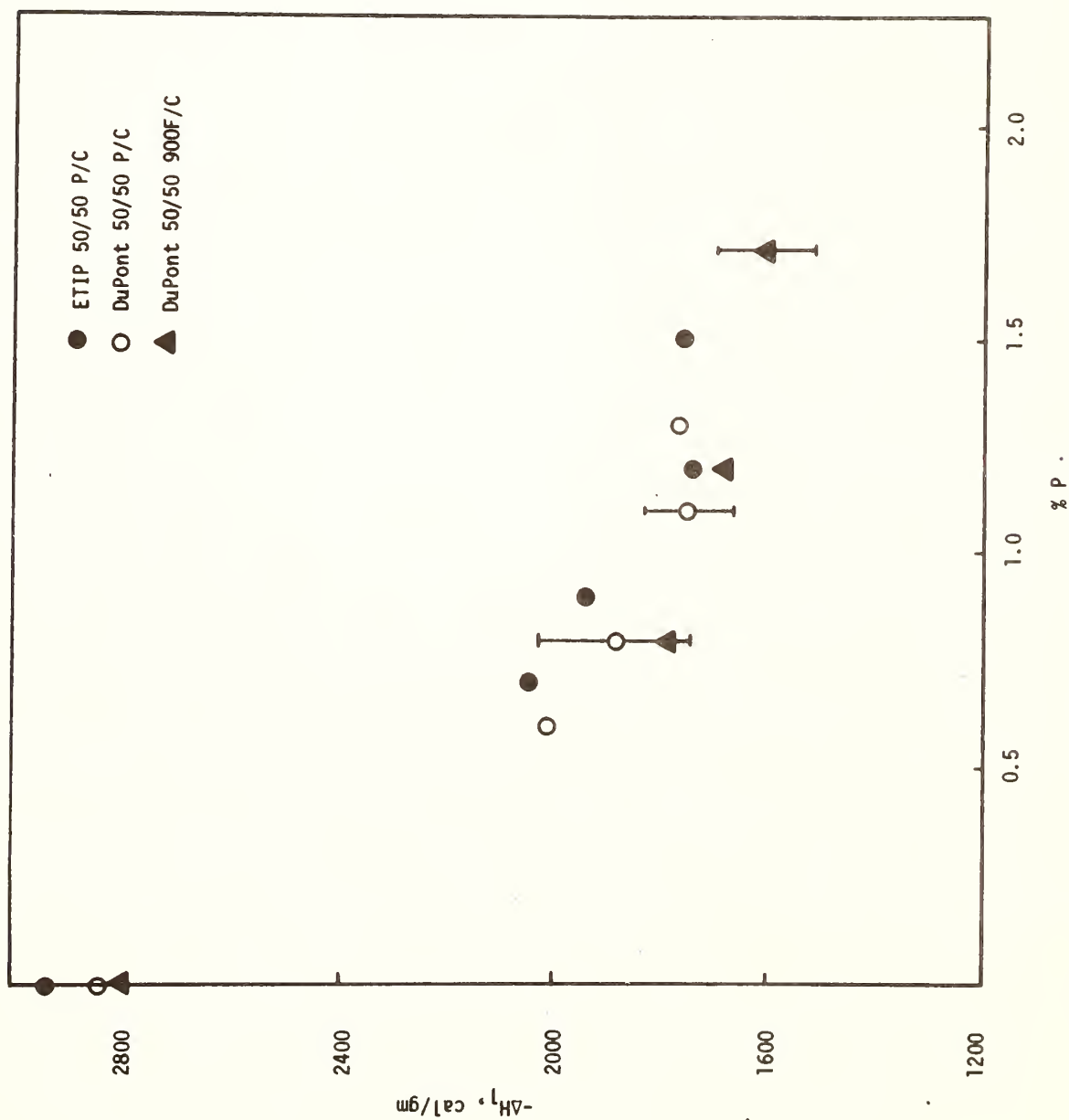


FIGURE 94. Variation of ΔH_1 with P content of THPC-CH₃NH₂ treated blends.

chemical structure does not vary. Only the THPC-CH₃NH₂ oligomer was found to have an inherent aesthetic property which may be difficult to overcome. The residual CH₃NH₂ proved to be very difficult to remove from the reaction mixture, probably due to the various equilibria involved, and consequently considerable discoloration was observed after the cure.

During the initial investigation of the THPC-MCC-100^(R) oligomer an attempt was made to evaluate this finish, using urea, in an application similar to that which would be encountered in commercial production. A series of laboratory experiments were carried out at SRRC duplicating the conditions which would be encountered in a pilot plant. During these examinations an unacceptable lack of durability of the finish was observed in the process wash following curing. This is demonstrated by the data in Table LXV.

In order to overcome this problem, the urea was replaced by a melamine derivative in the formulation. Use of Monsanto's MCC-200^(R) and 300 system produced a reasonably durable system as shown by the data in Table LXVI. This system also shows good fire retardant effectiveness in both the 45° angle and vertical tests. Because of the promise shown by this system a small scale pilot plant trial was carried out at SRRC. Three ten yard samples of fabric were treated at levels of 1.9, 2.8, and 3.9% phosphorus. The highest add-on passed the vertical burn test initially but failed after five laundering cycles. Elemental analysis of these fabrics indicated a major loss of phosphorus during laundering. Since the oligomer itself is stable to these conditions, and since the oligomer is water soluble, it is presumed that the loss of flame retardancy results from cleavage of bonds between the oligomer and the melamine resins.

Two other difficulties which were encountered in using the THPC/MCC-100^(R)/200/300^(R) finish that were not encountered in the corresponding urea system were a considerably harsher hand and a significant loss of tear strength. However, it was found that inclusion of Dow-Corning's Emulsion 1111^(R) hand modifier and resin extender into the formulation resulted in a distinct improvement in both hand and tear

TABLE LXV

Durability of MCC-100[®]/THPC/UREA
Finish on 50/50 Blend

<u>%H₂O₂ conc.</u>	<u>x⁽¹⁾ after cure</u>	<u>x, cold wash</u>	<u>x⁽²⁾ hot wash</u>	<u>x⁽³⁾ hot wash</u>
3.9	0.330	.263	.255	.065
9.7	0.328	.246	.256	.063

(1) weight percent

(2) one minute

(3) twenty minutes

strength.

To more completely define the nature of the durability problem encountered with the THPC-MCC-100^(R) adduct, samples of 50/50 polyester/cotton fabric were treated with variations of the MCC-100^(R)-THPC finish and scoured at the boil for four hours in a solution of 4g/l Orvus AB^(R) and 2.5 g/l soda ash. The scour baths were then neutralized with HCl to pH \sim 6.0 and the water stripped off using a rotary evaporator. The results of this scour are shown in Table LXVI.

The NMR spectra of the extraction residues were run in D₂O. The spectrum from the THPC-MCC-100/200/300^(R) sample contained two broad bands at 0.5 - 1.5 ppm indicating the presence of alkyl groups. It also contained a broad group of peaks at 2.5 and 3.0 ppm and a sharp peak at 4.1 ppm. These latter peaks are very similar to those observed in the NMR spectra of MCC-100^(R) and THPC respectively.

Two samples treated with the same THPC-MCC-100^(R)/urea system but cured under different conditions were also examined. The residue from Sample II cured at 160° for 2.5 minutes exhibited broad multiplets at 1.22 - 3.08 ppm and 3.54 - 4.0 ppm. The residue from the sample cured at 150° for 2.0 minutes yielded a spectrum which resembled that from the THPC-MCC-100/200/300^(R) system except for the absence of the broad bands at 0.5 - 1.5 ppm. These data would seem to indicate that at least in one case the lack of durability might be a function of poor fixation rather than hydrolytic instability of the oligomer.

In an attempt to improve the fixation of the THPC/MCC-100^(R) finish, MgCl₂ and MgCl₂-citric acid were tried as catalysts. Using equal molar concentrations in the pad bath the MgCl₂-citric acid complex appears to be the more efficient catalyst. The add-ons for the MgCl₂-citric acid bath ranged from 25.1 to 15.1 weight percent while those from the uncomplexed MgCl₂ went from 21.0 to 10.8 weight percent with the same dilutions. The performance of these materials in the vertical and 45° burns was similar although the MgCl₂-citric acid fabrics performed slightly better. These fabrics showed a small improvement in durability but this was not pursued because of the development of more effective approaches.

TABLE LXVI

Durability of Oligomeric THPC/MCC-100^(R) Finishes

Sample	Finish	Initial Wt. % Reagent	% Finish Loss
I	THPC/MCC-100/200/300 ^(R)	21.9	40.6
II	THPC/MCC-100 ^(R) /UREA ⁽²⁾	27.5	79.3
III	THPC/MCC-100 ^(R) /UREA ⁽³⁾	31.3	42.2

(1) Four hours at boil, 4g/l Orvus AB, 2.5 g/l soda ash

(2) 2.5 minutes at 160⁰

(3) 2.0 minutes at 150⁰

In one of these preparation of the oligomer was modified. Instead of adding the MCC-100^(R) dropwise to the THPC, the solutions were mixed rapidly producing a different pH for the condensation reaction and allowing less time for both condensation and hydrolysis. A solution of MCC-200^(R) and MCC-300^(R) was then added to the resulting oligomer solution along with a Sapamine^(R) softener. After curing at 16⁰C for 3 minutes this technique produced a fabric which exhibited good durability (ca. 3-4% weight loss) in a four hour soap/soda boil. However, the high resin content resulted in a finish with a very harsh hand and relatively poor tear strength.

The effect of the atmosphere over the precondensate reaction vessel, the pH of the precondensate baths, and the efficiency of several different resins were also investigated. The pad baths, add-ons, FF-5 results and some durability data from these experiments are summarized in Tables LXVII through LXXVII. On the basis of these results it would seem that the controlling factor still remains the % P in the finish and in this respect the resin employed has little effect on the efficiency of the retardant.

While the pH must be important in terms of bath stability and resin efficiency, in these limited results, the performance of the neutralized precondensate baths showed no significant improvement over a non-neutralized formulation. Similarly no significant effect was discerned from blanketing the reaction vessel with argon during the formation of the precondensate.

A initial^(R) investigation was also carried out with precondensates of THPC and THPS^(R) with trimethylphosphoramidate (MCC-100^(R) from Monsanto) and guanidine carbonate. Similar materials have been reported in a recent patent to Toyobo (U. S. 3,855, 349, December, 1974). The phosphorus content of these precondensates seem to be equivalent to the initial THPC/MCC-100/200/300^(R) adducts made at Clemson. Hence the efficiency of these systems is quite high as shown in Tables LXXXIII, LXXXIV, and LXXXV. However, the durability of the modified formulations also seems to be much better than that obtained in the eariler work. Typical pad bath formulations and flame retardant results obtained with

TABLE LXVII

Pad Bath THPC/MCC-100[®] (Prepared Under Non-Oxidizing Atmosphere)

100 ml of an 80% THPC solution
 100 ml of a 70% MCC-100[®] solution
 stir together under Argon for 45 minutes
 cool in an ice bath
 add a solution prepared by dissolving
 45 g MCC-200[®] in 45 ml of H₂O
 20 ml of a 10 wt % solution of Triton[®] X-100
 15 g Sapamine[®] APN
 200 ml H₂O

1 Dip, 1 Nip on lab pad

Dry 2 min at 150^oC
 Cure 4 min at 150^oC
 Wash 3 min in warm 2% Na₂ CO₃
 Oxidize 3 min in warm solution of
 20 ml 35 wt % H₂O₂
 6 g sodium silicate
 4 ml 40 wt % NaOH
 10 ml 10 wt % Triton[®] X-100
 H₂O to 1 liter of solution
 Rinse in cold water
 Dry 2 min at 150^oC

Results (on ETIP 50/50)

	<u>Approximate Add-on</u>	<u>FF-5 (initial)</u>
Bath (1)	22%	7.9 in.

TABLE LXVIII

Pad Bath THPS[®]/MCC-100[®] (Prepared Under Non-Oxidizing Atmosphere)

100 ml of a 70% THPS[®] solution
 100 ml of a 70% MCC-100[®] solution
 stir together under Argon for 45 min
 cool spontaneously
 add a solution prepared by dissolving
 22.5 g MCC-200[®] in 22.5 ml H₂O
 add
 35 ml of Aerotex[®] 23 Special
 15 g of Sapamine[®] APN
 20 ml of a 10 wt % solution of Triton[®] X-100
 200 ml of H₂O

Dry, Cure, etc. See Table LXVII

Results (on ETIP 50/50)

	<u>Approximate Add-on</u>	<u>FF-5 (initial)</u>
Bath (1)	20%	fail

TABLE LXIX

PAD BATH THPS^(R)/MCC-100^(R) NEUTRALIZED

100 ml of a 70% THPS^(R) solution
 100 ml of a 70% MCC-100^(R) solution
 stir together under Argon for 45 min
 cool spontaneously
 place in an ice bath
 neutralize solution to pH 7.2 with
 ~50 ml of a 20% NaOH solution
 add to the above solution a solution prepared by dissolving
 22.5 g MCC-200^(R) in 22.5 ml H₂O
 add
 35 ml of Aerotex^(R) 23 special
 20 ml of a 10 wt % solution of Triton^(R) X-100
 200 ml H₂O
 Dry, cure, etc. See Table LXVII

Results (on ETIP 50/50)

	<u>Approximate Wt % Add-on</u>	<u>FF5(initial)</u>	<u>4 Hr Scour Loss</u>	<u>Char</u>
Bath (1)	25%	fail	8%	50%

TABLE LXX

PAD BATH THPS^(R)/MCC-100^(R) NEUTRALIZED

100 ml of a 70% THPS^(R) solution
 100 ml of a 70% MCC-100^(R) solution
 stir together under Argon for 45 min
 cool spontaneously
 place in ice bath
 neutralize solution to pH 7.2 with
 ~50 ml of a 20% NaOH solution
 add to the above solution a solution
 prepared by dissolving
 22.5 g MCC-200^(R) in 22.5 ml H₂O
 then add
 35 ml Lyofix^(R) CHN
 15 g Sapamine^(R) APN
 20 ml of a 10% Triton^(R) X-100 solution
 200 ml H₂O

Dry, cure, etc. See Table LXVII

Results (on ETIP 50/50)

	<u>Approximate Wt % Add-on</u>	<u>FF5(initial)</u>	<u>4 Hr Scour Loss</u>	<u>Char</u>
Bath (1)	25%	fail	9%	50%

TABLE LXXI
PAD BATH THPOH/MCC-100 ^(R)

place in ice bath
 100 ml of a 70% THPS ^(R) solution
 add
 50 ml H₂O
 neutralize to pH 7.2 by slowly adding
 ~25 ml of a 20% NaOH solution
 add
 100 ml of a 70% MCC-100 ^(R) solution
 20 ml of a 20% solution of MgCl₂
 citric acid
 heat to 85°C under Argon for 1 hr
 strip on rotovap to dryness
 to the above oligomer, add a solution prepared by dissolving
 22.5 g of MCC-200 ^(R) in 22.5 ml H₂O
 add
 35 ml Lyofix ^(R) CHN
 15 g Sapamine ^(R) APN
 20 ml of a 10% solution of Triton ^(R) X-100
 add H₂O to bring total bath volume to 300 ml

Dry, cure, etc. See Table LXVII

Results (on ETIP 50/50)

<u>Approximate Add-on</u>		<u>FF5(initial)</u>	<u>4 Hr Scour Loss</u>	<u>Char</u>
Bath (1)	45%	fail	25%	25%
Bath (1) + 150 ml H ₂ O=Bath (2)	32%	fail		
Bath (2) + 150 ml H ₂ O=Bath (3)	22%	fail		
Bath (3) + 200 ml H ₂ O=Bath (4)	15%	fail		

TABLE LXXII

PAD BATH THPC/MCC-100/200/300 (R)

slowly add to

100 ml of an 80% THPC solution

100 ml of a 70% MCC-100 (R) solution

to the above solution, add

50 MCC-200 (R) dissolved in 200 ml H₂O

then add

8.7 g MCC-300 (R)

Dry: Group I fabrics dry at 85°C for 10 min

Group II fabrics dry at 165°C for 2 min

Cure at 165°C for 2.5 min

Wash 3 min in warm 2% Na₂CO₃

Oxidize 3 min in warm solution of

20 ml 35 wt % H₂O₂

6 g sodium silicate

4 ml 40 wt % NaOH

10 ml 10 wt % Triton (R) X-100

H₂O to 1 liter of solution

Reoxidize 3 min. in 3.5% H₂O₂

Rinse Group I fabrics in cold water

Rinse Group II fabrics for 20 min in hot water

Dry for 2 min at 165°C

Results (on ETIP 50/50)

<u>Approximate Add-on</u>		<u>FF5(initial)</u>	<u>4 Hr Scour Loss</u>	<u>Char</u>
GI Bath (1)	43%	4.7 in	10%	30%
Bath (1) + 200 ml H ₂ O=Bath (2)	28%	5.9 in	8%	40%
GII Bath (1)	41%	3.2 in	14%	40%
Bath (1) + 200 ml H ₂ O=Bath (2)	28%	4.3 in	10%	50%

TABLE LXXIII

PAD BATH THPC/MCC-100[®]/GUANIDINE CARBONATE

Dissolve

3 g Guanidine carbonate in 72 ml H₂O
add

128 g an 80% solution of THPC

31.3 ml of a 70% solution of MCC-100[®]

reflux the above solution for 1 hr
cool

to 200 g of the above oligomer, add

20 g Urea and

1 g solid NaOH dissolved in 80 ml H₂O

Dry, cure, etc. See Table LXXII. Group II conditions.

Results (on ETIP 50/50)

	<u>Approximate Add-on</u>	<u>FF5(initial)</u>	<u>FF5(After Scour)</u>	<u>4 Hr Scour Loss</u>
Bath (1)	37%	pass	pass	4.5%
Bath (1) + 100 ml H ₂ O=Bath (2)	22%	½ fail	fail	2.5%

TABLE LXXIV

PAD BATH THPC/MCC-100^(R)/GUANIDINE CARBONATE

Dissolve

3 g Guanidine carbonate in 72 ml H₂O

add

128 g of an 80% solution of THPC

31.2 ml of a 70% solution of MCC-100^(R)

reflux the above solution for 1 hr

cool

to 200 g of the above oligomer, add

10 g Urea

14 g MCC-200^(R) and1 g NaOH dissolved in 80 ml H₂O

Dry, cure, etc. See Table LXXII. Group II Conditions.

Results (on ETIP 50/50)

	<u>Approximate Add-on</u>	<u>FF5(initial)</u>	<u>FF5 After Scour</u>	<u>4 Hr Scour Loss</u>
Bath (1)	31%	pass	pass	3%
Bath (1) + 100 ml H ₂ O=Bath (2)	22%	½ fail	fail	2%

TABLE LXXV
PAD BATH THPS^(R)/MCC-100^(R)/GUANIDINE CARBONATE

Dissolve

3 g Guanidine carbonate in 54 ml H₂O

add

146.3 g of a 70% solution of THPS^(R)

31.3 ml of a 70% solution of MCC-100^(R)

reflux the above solution for 1 hr

cool

to 200 g of the above oligomer, add

20 g Urea

1 g NaOH dissolved in 80 ml H₂O

Dry, cure, etc. See Table LXXII. Group II Conditions.

Results (on ETIP 50/50)

<u>Approximate Add-on</u>		<u>FF5(initial)</u>	<u>4 Hr Scour Loss</u>	<u>Char</u>
Bath (1)	27%	pass	5%	40%
Bath (1) + 100 ml H ₂ O=Bath (2)	19%	fail	4%	25%
Bath (2) + 100 ml H ₂ O=Bath (3)	14%	----	3%	20%
Bath (3) + 100 ml H ₂ O	10%	----		

TABLE LXXVI

THPS[®]/MCC-100[®]Aerotex[®]23 ON ETIP 50/50 POLYESTER/COTTON

Preparation of precondensate

Mix 146.3 g THPS[®] (70% solution)
 31.3 ml 70% MCC-100^R
 11.7 g Aerotex[®]23 special
 54 g H₂O

Reflux for 1 hour

Bath: Dissolve 20 g Urea
 1 g NaOH
 in 80 ml H₂O
 Add 200 g of the above precondensate

Dry: 2 min at 165°C

Cure: 4 min at 165°C

Afterwash: 3 min with agitation in a warm 2% Na₂CO₂ solution

Oxidize: 3 min with agitation in a warm solution of (per liter of soln)

20 ml 35% H₂O₂
 6 g sodium silicate
 4 ml 40% NaOH
 10 ml 10% Triton[®]X-100

Dry: 2 min at 150°C

Test Results

<u>Add-on</u>	<u>FF5</u>	<u>% Loss 4 Hr Scour</u>	<u>% Char</u>
27	3/4 (3.9 in)	10	30
18	1/3 (3.7 in)	7	20

TABLE LXXVII
THPS^(R)/MCC-100/200^(R) ON ETIP 50/50 POLYESTER/COTTON

Preparation of precondensate

Dissolve 7 g MCC-200^(R)
in 70 ml H₂O

Add 146.3 g THPS^(R)
16.5 ml 70% MCC-100^(R)

Reflux for 1 hour

Bath: 200 g of the above 50% precondensate

Add 20 g Urea and 1 g NaOH

Dissolved in 80 ml H₂O

Dry, cure, etc. See Table LXXVI

Test Results

Add-on

FF5

33%

4/4 (2.9 in)

25%

1/4 (3.7 in)

TABLE LXXVIII
PAD BATH THPS^(R)/CARBAMATE/MCC-200^(R)

Dissolve

7 g MCC-200^(R) in 49 ml H₂O

add

146.3 g of a 70% solution of THPS^(R)

49.5 ml of a 50% solution of Protorez^(R) CHD

reflux the above solution for 4 hr

cool

to 200 g of the above oligomer, add

48 g MCC-200^(R) dissolved in

60 g H₂O

1 Dip, 1 Nip on lab. pad.

Dry 2 min at 165°C

Cure 4 min at 165°C

Afterwash: post-oxidize as in Table LXXVI

Results (on ETIP 50/50)

	<u>Add-on</u>	<u>FF5</u>
Bath (1)	38%	3.31, 3.40, 4.80 ⁽¹⁾
Bath (1) + 100 ml H ₂ O=Bath (2)	28%	2.76, BEL, 6.77 ⁽²⁾

⁽¹⁾After 50 home launderings

⁽²⁾FF5 Initial

these oligomers are given in Table LXXVI and LXXVII. These results show that the precondensate can be used to impart self-extinguishing properties to 50/50 blend fabrics but that high add-ons will be required to achieve successful performances in FF-5. For this reason, attempts were made to find additional components which could be added to the precondensate formulations to improve their retardant efficiency and the inherent aesthetics of the fabrics.

One approach to increasing the efficiency of a precondensate finish is to decrease the fuel content of the resin used in fixation. In practice this can be accomplished by the use of an ammonia rather than a resin cure. An attempt was made to ammonia cure several of the precondensates listed in Tables LXVII through LXXVIII using a very crude ammoniating chamber at Clemson. In general a high phosphorus to nitrogen ratio in the precondensate was necessary to obtain an effective ammonia cure. The nature of the nitrogen containing components of the precondensate did not appear to be very important in terms of curing efficiency. Those precondensates which could be successfully ammonia cured required about 20% less of an add-on to pass an initial FF-5 on the ETIP 50/50 PET/Cotton blend fabric. These very preliminary results indicated that ammonia curing could be a very effective means of applying these phosphorus containing precondensates.

Another approach which was tried involved using a carbamate in the precondensation reaction. It was felt that the formation of a more linear oligomer would result in a considerably improvement in hand over the highly cross-linked three-dimensional oligomers which had been made. The oligomer reaction mixture, pad bath formulation; FF-5 and durability data for this precondensate is presented in Table LXXVIII. The vertical flame test performance of this precondensate was found to be comparable to that of the other oligomers of this type as shown by the data in Table LXXVII. In addition the anticipated improvement in hand and tear strength was subjectively observed.

There are two important conclusions which can be drawn concerning oligomeric phosphonium structures based on the data presently available. The most important being that they have great potential for flame

retarding polyester/cotton blend fabrics but this potential has not yet been fully realized. Secondly, despite the fact that their mode of flame retardant action is fairly independent of the oligomer chemical structure, there are significant differences in both fabrics aesthetics and phosphorus content which are dependent on the precondensate structure.

FLAME RETARDANT SYSTEMS BASED ON BROMINE ALONE

Unlike the phosphorus systems, relatively few treatments have been designed in which bromine is the only flame retardant species. To date the only finish of this type which has achieved any measure of success in textile applications is that based on decabromodiphenylene oxide in conjunction with an antimony oxide synergist (FR P-44[®] from White Chemical Company). Although basically an efficient flame retardant, this system suffers from problems due to the flammability and aesthetic properties of the acrylic binder, a lack of durable press properties, the shade changes which occur when used in dark colors and certain processing problems such as build-up on the pad rolls. A series of investigations was, therefore, carried out in an attempt to characterize the flame retardant action of P-44[®] and design modifications which might be able to circumvent some of its problems while preserving its high molar efficiency.

1. Calorimetric Evaluation of FR P-44[®]

Three series of samples treated with P-44[®] were investigated calorimetrically. These included a 100% cotton and 50/50 and 65/35 polyester/cotton blends each treated at five levels of add-on ranging from 2.5 to 10.50% Br. The isoperibol results are tabulated in Table LXXIX. All these samples exhibited a substantial amount of after-glow. Residue yield (%R) indicated that the retardant action was predominantly in the vapor phase. The heat-release values from the isoperibol calorimeter were plotted vs Br% content as shown in Figure 95. In all three series (including 100% cotton), the "threshold" was reached at approximately 8 to 10% Br. The most striking observation was probably the retardant effect exhibited by this retardant on 100% cotton. Its effectiveness on 100% cotton was essentially the same as on the two blends. This can be seen more clearly when the net heat reduction of each treated sample is plotted vs %Br as shown in Figure 96. The net heat reduction is given by the difference

TABLE LXXIX

Isoperihol Data of the Decabromodiphenyl Oxide (White Chemical) Treated Polyester/Cotton Blends

Sample	% Br	% R	Rate, cal/sec-cm	$-\Delta H_f$, cal/gm	$\Delta H_f - (\Delta H_f)_{\text{control}}$, cal/gm
100% Cotton	control	---	79.9	3334	0
	2.01	2.7	62.3	2861	473
	3.68	5.1	52.7	2443	891
	3.04	3.2	54.5	2478	856
	4.26	3.1	56.1	2576	758
	6.23	5.9	49.5	2093	1241
	7.19	30.4 \pm 6.4	41.3 \pm 4.6	1545 \pm 192	1789
50/50 PET/Cotton	control	6.6	62.0	2767	0
	1.89	7.6	57.1	2394	373
	4.00	5.6	46.8	2150	610
	4.15	6.7	45.5	2179	588
	5.91	24.5 \pm 12.5	35.1 \pm 4.3	1424 \pm 343	1343
	6.27	32.4	30.1	1189	1578
65/35 PET/Cotton	control	8.7	54.2	2846	0
	1.67	9.7	51.8	2323	523
	3.73	10.5	63.6	2154	692
	5.22	9.7	43.9 \pm 5.3	2000	846
	5.68	11.4	37.8	1826	1020
	6.30	12.9	35.6 \pm 3.6	1633 \pm 114	1213

¹ All samples exhibited substantial after-glow.² Large variations from run to run, average of three runs.

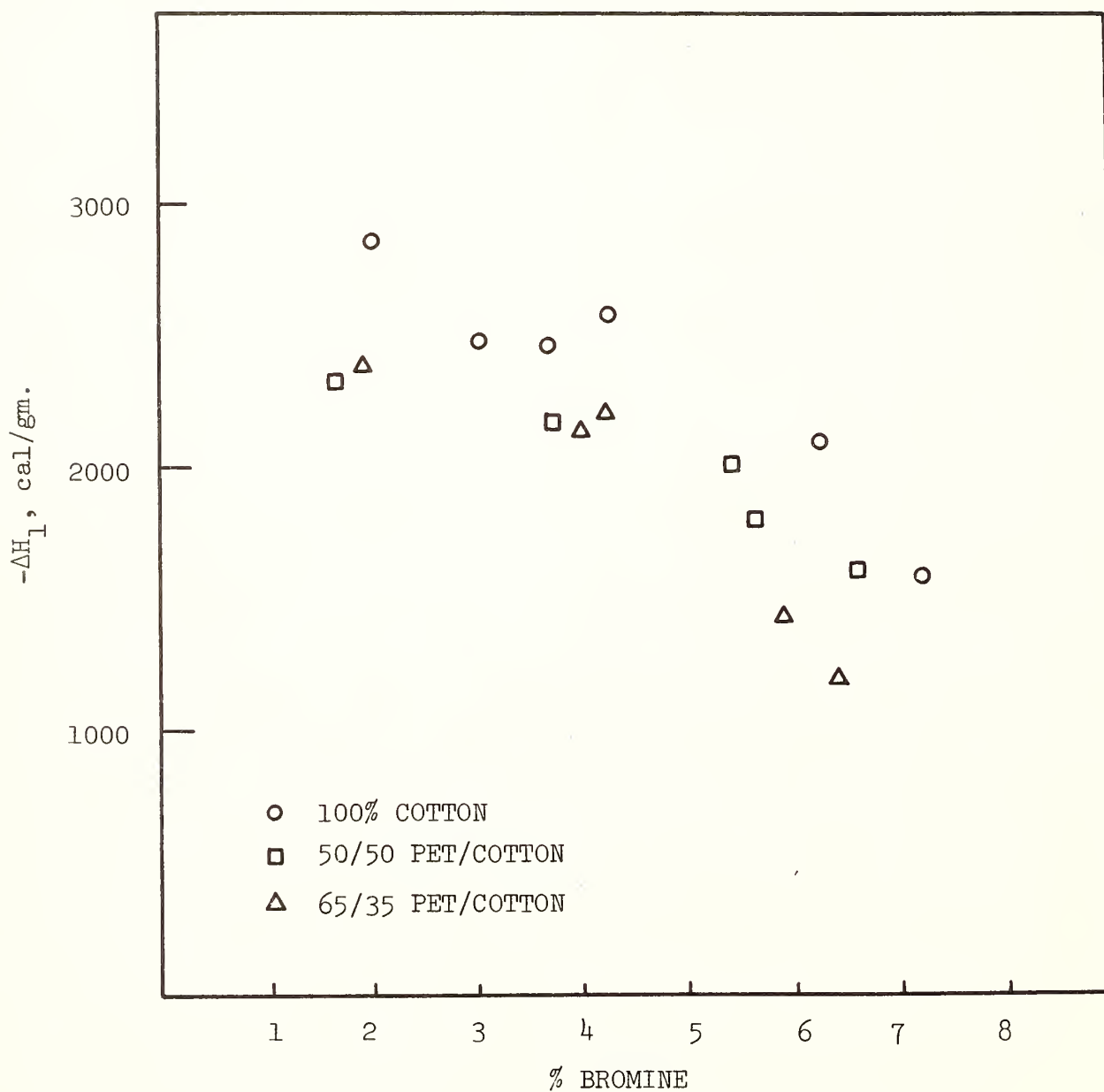


FIGURE 95. Heat release of decabromodiphenyl oxide treated blends.

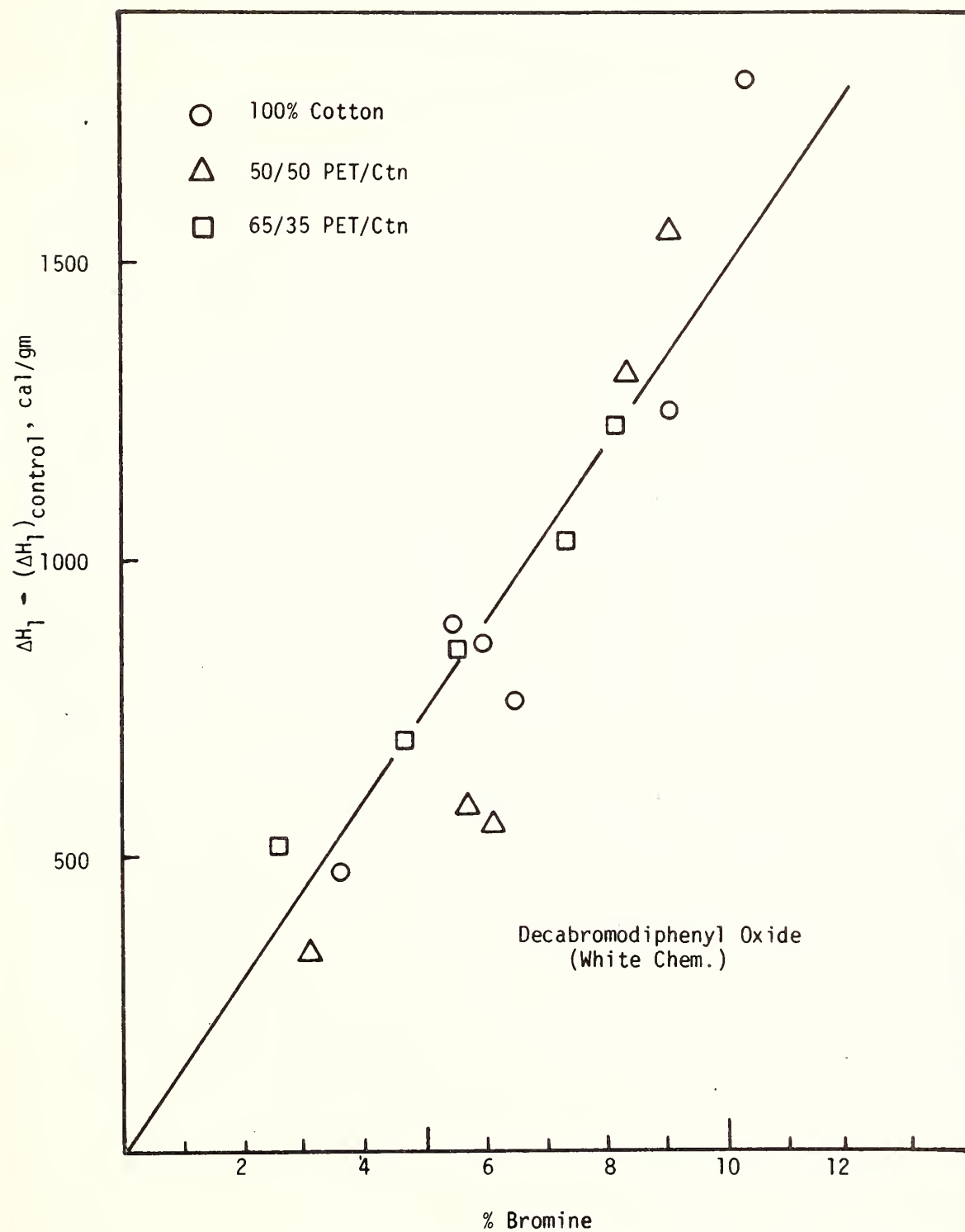


FIGURE 96. Net heat reduction from decabromodiphenyl oxide treated PET/cotton blends.

between the heat release of the treated samples and that of the control ($\Delta H_1 - \Delta H_{1, \text{control}}$). Figure 96 shows that the net heat reductions of all treated samples are a single function of %Br content, indicating that the effectiveness on cotton is essentially the same as that on polyester.

The decomposition temperature of decabromodiphenyl oxide is 310°C , which is very close to that of cotton, assuming that there is no solid-phase action by the retardant (Br) on cotton. The absence of solid-phase action on cotton may be the key to the effectiveness of this retardant. However, this lack of condensed phase activity could not be verified by TGA as shown by the data in Table LXXX.

Unfortunately, it has been found that it is difficult to draw generalized conclusions on the basis of specific data such as these. This is demonstrated by the results obtained from a second set of fabrics treated on a different occasion than those above and using a different lot of FR P-44[®]. Bromine contents of all the P-44[®] treated fabrics were analyzed using an x-ray technique and the data compiled in Table LXXXI. Finish contents calculated from wet pick-ups are also included in Table LXXXI. Decabromodiphenyl oxide (DBDPO) contents were calculated from the analyzed bromine content for each sample and are shown in Column 3 of Table LXXXI. The DBDPO content in the finish (% DBDPO/% Finish) is shown in Column 4. These results indicate that the DBDPO content in the P-44[®] finish can vary with the treatment as well as with the type of fabric used. In the first treatment, DBDPO contents in the finish are consistently about 66% for all fabrics treated, whereas, in the second treatment, DBDPO contents in the finish are 50% for 100% cotton and 46% for the 50/50 blend. However, the DBDPO contents in the finish for a given fabric in a given treatment are consistent. Figure 97 shows a plot of analyzed bromine contents vs % finish. Presumably the variation of DBDPO contents in the finish would affect the balance of bromine and antimony contents present; and this is generally regarded as the key to the efficiency of this type of retardant.

An additional set of anomolous bromine analyses was encountered in experiments to determine the minimum levels of P-44[®] application

TABLE LXXX
Thermal Analysis of FR P-44[®] Finished Fabrics

%Br (1)	Ti (2)	WL (3)	Ts (4)	WLs (5)	Tm _i , Tm _s (6)		R (7)
<u>100% Cotton</u>							
3.6	312	.794	--	--	337		.204
5.5	304	.735	--	--	327		.172
6.0	307	.703	--	--	327		.173
6.6	313	.704	--	--	335		.191
9.1	291	.686	--	--	315		.178
10.4	299	.660	--	--	324		.204
<u>50/50 Cotton/Polyester</u>							
3.1	328	.393	349	.422	345	424	.156
5.8	312	.360	328	.424	329	395	.189
6.1	318	.338	335	.394	337	403	.229
8.4	303	.366	322	.385	320	385	.239
9.1	306	.335	320	.419	323	378	.148
<u>65/35 Cotton/Polyester</u>							
2.6	333	.250	352	.539	352	433	.200
4.7	327	.259	344	.538	346	427	.165
5.6	328	.234	345	.493	346	427	.223
7.4	324	.272	342	.529	343	424	.171
8.2	323	.242	338	.515	341	416	.193

(1) %Br estimated on the basis of weight % add-on of finish.

(2) Onset temperature of initial weight loss (cellulose fraction)

(3) % weight loss during initial weight loss

(4) Onset temperature of secondary weight loss (polyester fraction)

(5) % weight loss occurring during secondary weight loss

(6) Temperatures of derivative maxima for initial and secondary weight losses

(7) Residue at 500°C

TABLE LXXXI
BROMINE CONTENTS OF FABRIC SAMPLES TREATED WITH P-44 ^(R) RETARDANT

% Finish	% Br Analyzed	% DBDPO* calcd.	% DBDPO/% Finish
<u>Treatment #1</u>			
100% Cotton			
4.32	2.01	2.41	0.56
6.58	3.68	4.42	0.67
7.91	3.04	3.65	0.46
7.14	4.26	5.11	0.72
10.87	6.23	7.48	0.69
12.48	7.19	8.63	0.69
50/50 PET/Cotton			
3.71	1.89	2.27	0.61
6.90	4.00	4.80	0.70
7.34	4.15	4.98	0.68
10.08	5.91	7.08	0.70
10.91	6.27	7.52	0.69
65/35 PET/Cotton			
3.08	1.67	2.00	0.65
6.73	3.73	4.48	0.65
8.90	5.22	6.26	0.69
9.88	5.68	6.82	0.69
			Ave. 0.66 ± 0.07
<u>Treatment #2</u>			
100% Cotton			
5.80	2.64	3.17	0.55
6.35	2.70	3.24	0.51
9.54	4.18	5.02	0.53
12.24	4.27	5.13	0.42
13.67	4.94	5.93	0.43
14.57	6.54	7.85	0.54
			Ave. 0.50 ± 0.06
50/50 PET/Cotton			
5.98	2.38	2.86	0.48
9.96	3.79	4.55	0.46
13.20	4.97	5.97	0.45
16.41	6.34	7.61	0.46
18.04	6.88	8.26	0.46
			Ave. 0.46 ± 0.01

* Decabromodiphenyl Oxide

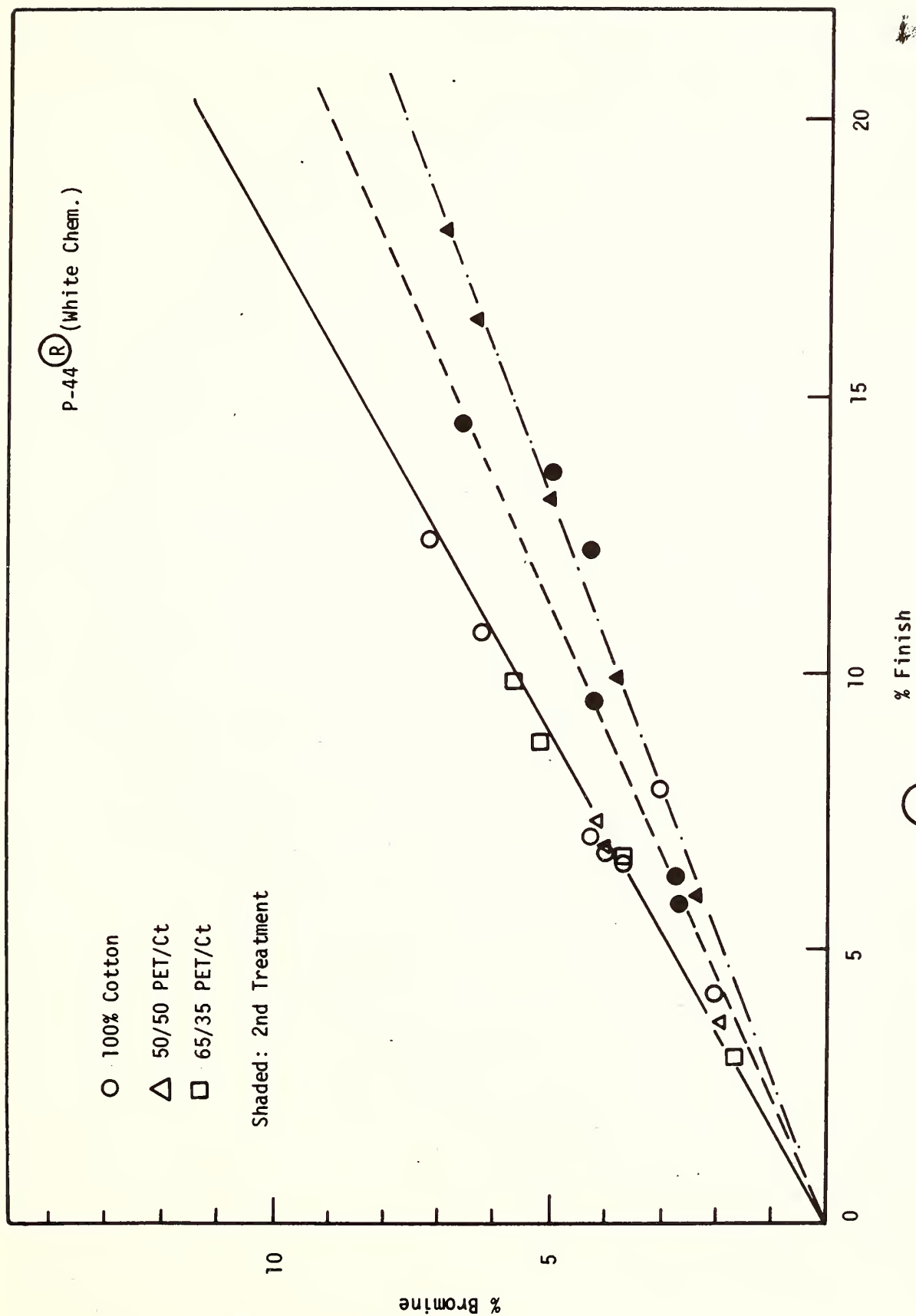


FIGURE 97. Bromine contents of P-44[®] treated fabrics.

necessary to achieve satisfactory performance in FF 3-76 and on the MAFT. Samples of 50/50 polyester/cotton blend fabric were treated with P-44^(R) at four different levels of application, and each laundered 20 and 50 times.

2. Application of FR P-44^(R) with Durable Press Resins

Since the calorimetric evaluation of P-44^(R) had shown a high level of efficiency, it seemed that attempts to improve its utility were in order. A series of studies were therefore undertaken in cooperation with Dr. Vladimir Mischutin of White Chemical Corporation. After some initial laboratory experimentation, the formulations given in Table LXXXII were developed using a glyoxal resin (Permafresh 113B^(R)) either in the flame retardant bath or as a top finish. These formulations were evaluated in a pad-dry-cure operation using the pilot plant at SRRC. Three styles of polyester/cotton blends were used (two 50/50 blends and one 65/35 blend) along with one 50/50 polyester/rayon. The results are shown in Table LXXXIII. After examination of the samples, the group at White Chemical Corporation concluded that treatments I, II, and III were over cured thus resulting in lowered durability due to decomposition of the resin. However, because of the apparently deleterious effect of the permanent press resin coupled with the poor hand of the fabrics and the build-up observed in the pad rolls during processing, this approach was abandoned.

3. Application of FR P-44^(R) with a Bromine-containing Latex

Since many of the problems encountered in the use of FR P-44^(R) are related to the necessity for high add-ons, an effort was made to modify the application formulation to reduce the amount of chemical required. It was thought that part of the basis for needing so much flame retardant was the flammability of the acrylic binder used; thus it was reasoned that the use of a flame resistant acrylate would be beneficial.

TABLE LXXXII

P-44^(R) FORMULATIONS WITH PERMANENT PRESS TREATMENTS

<u>Treatment</u>	<u>Component</u>	<u>Wt. % in Pad Bath</u>
I	Water	40.0
	Carbowax 400 ^(R)	2.0
	P-50 softener	3.0
	Rhoplex TR-485 ^(R)	10.0
	P-44 ^(R)	45.0
	Resin	(1)
II	Water	44.0
	Nyacol 1550 ^(R)	9.0
	Carbowax 400 ^(R)	2.0
	P-50 softener	3.0
	Rhoplex TR-485 ^(R)	10.0
	P-44 ^(R)	32.0
III	Resin	(1)
	Water	25.0
	Carbowax 400 ^(R)	2.0
	P-50 softener	3.0
	Rhoplex TR-485 ^(R)	10.0
	P-44 ^(R)	45.0
IV	Permafresh 113B ^(R)	15.0
	Water	27.0
	Nyacol 1550 ^(R)	9.0
	Carbowax 400 ^(R)	2.0
	P-50 softener	3.0
	Rhoplex TR-485 ^(R)	10.0
	P-44 ^(R)	32.0
	Permafresh 113B ^(R)	17.0

TABLE LXXXII (con't.)

<u>Treatment</u>	<u>Component</u>	<u>Wt. % in Pad Bath</u>
V	Water	39.0
	Nyacol 1550 ^(R)	9.0
	Carbowax 400 ^(R)	2.0
	P-50 softener	3.0
	Rhoplex TR-485 ^(R)	15.0
	P-53 ^(R)	32.0

(1) Top treated with 15% Permafresh 113B^(R), 3% catalyst X-4^(R) and 82% water.

TABLE LXXXIII

FLAMMABILITY OF PERMANENT PRESS/P-44[®] TREATMENTS

Treatment	Blend	Scoured	Average Char Length (FF 3-71)	
			Initial	50 washes
I	50/50 PET/Cotton	yes	3-1/8 in	fail
		no	3-1/4 in	fail
	65/35 PET/Cotton	yes	3-5/8 in	fail
		no	3-3/8 in	fail
	50/50 PET/Rayon	yes	3-1/2 in	fail
		no	3-3/4 in	fail
II	50/50 PET/Cotton	yes	3-3/4 in	fail
		no	3-1/2 in	fail
	65/35 PET/Cotton	yes	4-1/2 in	fail
		no	4-1/4 in	fail
	50/50 PET/Rayon	yes	3-3/8 in	6-1/2"
		no	4 in	fail
III	50/50 PET/Cotton	yes	3-1/4 in	fail
		no	3-1/4 in	fail
	65/35 PET/Cotton	yes	3-3/4 in	fail
		no	4-1/4 in	fail
	50/50 PET/Rayon	yes	3-1/4 in	fail
		no	2-3/4 in	fail
IV	50/50 PET/Cotton	yes	3-1/2 in	4-5/8"
		no	3-1/2 in	4"
	65/35 PET/Cotton	yes	4-1/2 in	fail
		no	3-5/8 in	fail
	50/50 PET/Rayon	yes	3-1/2 in	5-1/8"
		no	3-5/8 in	5-7/8"

TABLE LXXXIII (con't.)

Treatment	Blend	Scoured	Initial	50 washes
V	50/50 PET/Cotton	yes	3-1/2 in	5-3/4"
		no	4-1/2 in	fail
	65/35 PET/Cotton	yes	3-3/4 in	fail
		no	4-1/4 in	5-3/8"
	50/50 PET/Rayon	yes	3-3/8 in	fail
		no	4-1/2 in	fail

A series of experiments was therefore initiated to design and develop suitable flame retardant latexes. After screening a number of monomers, emulsion polymerizations of 2,3-dibromopropyl acrylate (DBPA, Great Lakes Chemical AE-59) and 2,4,6-tribromophenoxyethyl acrylate (TBPOEA) were carried out. Of these, the DBPA polymer, P(DBPA), was adjudged the best commercial candidate and attention was focused on it. Through the cooperation of the Charles S. Tanner Division of Ciba-Geigy Corporation a commercially feasible preparation for a latex having the characteristics given in Table LXXXIV was developed. This material has now been designated as Dur-O-Cry[®] BL-1 by Charles S. Tanner. Attempts to incorporate P(DBPA) into the P-44[®] formulation led to a marked increase in flame retardant efficiency but decreased durability to laundering. In order to improve the durability, a small amount of TMM was added to the formulation (10% on the weight of the latex).

It is also found that this formulation could be made compatible with a glyoxal resin (Permafresh[®] LF) to impart both flame resistance and durable press characteristics at the same time. When applied in a normal pad-dry-cure process with a reactive silicone softener this system produces a durable flame retardant finish with good permanent press properties and hand. Strength losses are also minimized as shown by the data in Table LXXXV. The level of finish required to pass FF 3-71 is less than that previously recommended for P-44[®] even though the finish now contains the durable press resin. An additional processing advantage was also seen in the observation that there was no build-up of flame retardant on the pad rolls under laboratory application conditions. Many P-44[®] formulations do produce a build-up even under laboratory conditions.

On the basis of these promising results, a mill trial was conducted at the Clearwater Finishing Plant of United Merchants & Manufacturers using the formulation in Table LXXXVI.

The fabrics used included 150 yds of the standard 50/50 poplin with a normal preparation (scouring and bleaching), a 50 yd sample of the same fabric which had been re-soaped at Clearwater and a 50 yd sample which had been rescoured at SRRC using a desizing agent and an organic scouring agent. These modifications in fabric preparation were

TABLE LXXXIV
CHARACTERIZATION OF DBPA EMULSION POLYMER (1)

% Solids	40
Viscosity	50 cps
Tg (by DSC)	-10°C
Ave. particle size	0.13 μ
% Br (theoretical)	21

(1) Dur-o-cryl[®] BL-1 from C. S. Tanner

TABLE LXXXV

PHYSICAL PROPERTIES OF 50/50 BLEND TREATED WITH FR P-44^(R) AND P(DBPA)

Add-on	Tearing strength (lbs)	Tensile strength (lbs)	Wrinkle Recovery (W&F)	Char Length (in)		Bromine Content	
				Initial	50 Launderings	Initial	50 Launderings
0	79 x 67	7.3 x 6.4		BEL			
30.5 ⁽²⁾			282	4/4	2.5(0) ⁽³⁾		
21.8 ⁽²⁾			---	4/4	2.4(0) ⁽³⁾	1/2	6.6(11) ⁽³⁾
(1)	68 x 57	7.2 x 5.6		4/4	2.5(0) ⁽³⁾	8.7	6.4
(1)				4/4	2.4(0) ⁽³⁾	6.5	4.7
				4/4	2.4(0) ⁽³⁾	6.0	4.2

319

(1) Mill run

(2) Lab run

(3) After flame, sec.

TABLE LXXXVI

PAD BATH FORMULATION FOR P-44[®] WITH P(DBPA) BASED ON 91% WET PICK-UP

Reagent	weight (lbs)	volume (gal)
FR P-44 [®] (1)	135.2	8.44
Dur-o-cryl [®] BL-1 (2) (40% solids)	44.6	4.31
Trycol [®] OP-407 (3)	2.6	0.28
Permafresh [®] LF	31.1	3.27
Catalyst X-4 (4)	5.0	0.50
D-C 1111 Emulsion [®] (5)	17.9	2.14
D-C 182 A [®] (5)	1.8	0.22
D-C 149 [®] (5)	1.8	0.22
TMM (6)	1.8	0.22
Acetic acid (glacial)	1.8	0.22
Water	144.7	<u>17.34</u>
		36.94 gal

(1) White Chemical Company

(2) Chas. S. Tanner Company

(3) 40 mole ethoxylated octaphenol derivative, Emery Industries

(4) 40% $Zn(NO_3)_2$ from Sun Chemical Company

(5) Dow Corning Corporation

(6) Monsanto Chemical Company

included since work at SRRC had indicated a significant improvement in both hand and fire resistance achieved with the THPC[®]- Urea - P(VBr/VCl) finish after more extensive scouring.

After this first 250 yds of fabric had been padded, approximately 5 gallons of water were added to the pad bath and an additional 150 yds of the standard fabric with the normal preparation were padded. During this operation no significant build-up of material was noted on the pad rolls, even though the range was stopped off twice with several minutes standing time in each instance. The pad was also found to clean easily with only running water after the run was completed.

After padding, the fabric was passed through a 75 ft. tenter frame with temperatures of 233⁰F, 250⁰F and 230⁰F in the three boxes using a running speed of 50 yds per minute. The fabric was then cured for 3 minutes at 310⁰F in a loop oven, soaped in an open width soaper and dried. This produced a set of fabrics with good color, strength, hand and flame resistance and acceptable permanent press characteristics. These properties are demonstrated by the data in Table LXXXV. The only problem observed at this point was a dusting phenomenon which could be detected upon tearing the fabrics having the higher add-on levels.

After removing samples of fabric for further testing, the remainder of the material was printed using pigment colors and a flame retardant binder. The print was somewhat mealy, but it otherwise processed well. It was felt that this problem could be fairly easily overcome.

More significant was the finding that the dusting phenomenon apparently represented an instability of the treatment toward mechanical agitation which was reflected in durability testing. Subjection of these fabrics to a 4 hour soap-soda boil produced no significant decrease in their flame resistance, indicating a high degree of hydrolytic stability of the finish. However, when these fabrics were subjected to home laundry conditions, a significant loss of bromine occurred (Table LXXXV) and the samples failed the vertical test. Experiments were carried out to determine the cause of this low durability. Changes in the resin, catalyst and cure conditions which appear to improve the

durability of this finish have been made in the laboratory and a second mill trial scheduled for early September, 1976.

4. Application of Other Bromine-containing Flame Retardants

Although no other bromine systems have been developed to the same point as P-44[®], there are several which have been screened to determine their potential for further development. One of the most promising of these is an experimental material of unreported structure designated as Citex[®] BT-93 by Cities Service Company. This material contains 67% aromatic bromine, has good thermal and light stability, and low toxicity. It is supplied as a pale yellow powder (ca. 1 μ particle size) and is reported by Cities Service to have a high flame retardant efficiency.

Samples of Citex[®] BT-93 were dispersed in water using the formulation in Table LXXXVII and applied to 50/50 blend fabric using the process outlined in Table LXXXVIII. Attempts were also made to apply the Citex[®] BT-93 with the P(DBPA) but the pad bath was found to be unstable to the shear encountered during padding.

Colloidal antimony pentoxide was also evaluated as a synergist for Citex[®] BT-93 using the formulation in Table LXXXIX. The results are tabulated in Table XC. All of the samples appeared to be covered with a fine yellow powder which could be removed mechanically although the finish was found to be durable to 50 home launderings. The level of finish required to pass FF 3-71 was comparable to that required of decabromodiphenylene oxide when both are used in combination with an antimony oxide. A comparison of the levels required to pass FF 3-71 without antimony was not possible since a sufficiently concentrated bath of neither compound could be made.

The technique of combining a bromine/antimony oxide flame retardant with a bromine-containing latex binder appears to be applicable to many bromine systems. Preliminary results indicate that pentabromodiphenylene oxide (PBDPO, Cav-gard FRR 3-39[®], Cavedon Chemical Company) can be used as the flame retardant either with the P-44[®]/P(DBPA)

TABLE LXXXVII

EMULSIFIER FORMULATION

0.5 wt %	Tamol SN [®] (dispersing agent)
0.3 wt %	Cellose [®] (hydroxyethyl cellulose)
2.0 wt %	Triton W-30 [®] (sodium alkaryl ether sulfate)
balance	Water

TABLE LXXXVIII
APPLICATION OF CITEX[®] BT-93 TO 50/50 BLEND FABRIC

<u>Bath:</u>	100 g	50% dispersion BT-93
	1.68 g	Trycol OP-407 [®] (1) (40 mole octaphenol polyethylene oxide)
	23.6 g	Dur-o-cryl XWC [®] (acrylic emulsion)(2)
	1.2 g	MCC-200 [®] (trimethylol melamine)(3)
	1 g	Acetic acid
	53 g	H ₂ O
	18 g	Permafresh LF [®] (unbuffered glyoxal resin)(4)
	2.9 g	40% Zn (NO ₃) ₂ (4)
<u>Dry:</u>	10 min.	@ 85°C
<u>Cure:</u>	4 min.	@ 165°C
<u>Wash:</u>	3 min.	with agitation in hot 2% Na ₂ CO ₃
<u>Dry:</u>	10 min.	@ 85°C
<u>Weight % add-on:</u>	22	

(1) Emery Industries

(2) Ciba-Geigy

(3) Monsanto Chemical Company

(4) Sun Chemical Company

TABLE LXXXIX
CITEX[®] BT-93 AND Sb₂O₃ ON 50/50 BLEND FABRICS

<u>Bath:</u>	100 g	50% dispersion BT-93
	1.68 g	Trycol OP-407 [®] (1) (40 mole octaphenol (polyethylene oxide))
	23.6 g	Rhoplex TR-485 [®] (2) (self-cross-linking acrylic emulsion)
	1.2 g	MCC-200 [®] (trimethylol melamine) ⁽³⁾
	1 g	Acetic acid
	55.5 g	Nyacol A-1530 [®] (30% colloid Sb ₂ O ₃) ⁽⁴⁾
	18 g	Permafresh LF [®] (unbuffered gloxal resin) ⁽⁵⁾
	2.9 g	40% Zn (NO ₃) ₂ ⁽⁵⁾
	20 g	H ₂ O
<u>Dry:</u>	10 min.	@ 85°C
<u>Cure:</u>	4 min.	@ 155°C
<u>Wash:</u>	3 min.	with agitation in hot 2% Na ₂ CO ₃
<u>Dry:</u>	10 min.	@ 85°C
<u>Weight % add-on:</u>	26	

Note: Colloidal Sb₂O₃ used is not compatible with Dur-o-cry XWC

(1) Emery Industries

(2) Rohm and Haas

(3) Monsanto Chemical Company

(4) Nyacol Inc.

(5) Sun Chemical Company

TABLE XC

CHARACTERIZATION OF 50/50 BLEND FABRICS TREATED WITH CITEX ^(R) BT-93

	BT-93	BT-93 + Sb ₂ O ₃
Weight % Add-on	22.5	19.6
FF 3-71		
Char Length (cm)		
(fill only)	25	10.1 (9.7, 13.5, 8.2, 9.1)
Afterflame (sec)	14.5	2.0
% Br	10.5	6.0
50 HL	9.5	

formulation or with colloidal Sb_2O_5 and P(DBPA). The addition of a small amount of the PBDPO to the P-44[®]/P(DBPA) seems to be a viable way to increase the bromine content of the fabric without adversely affecting hand since PBDPO appears to thermosol into the fabric. When PBDPO is used alone it tends to give a somewhat greasy hand to the fabric but the presence of the P(DBPA) alleviates this problem.

Similarly, a number of bromine-containing monomers studied by radiation grafting appear to be suitable candidates for forming bromine containing latex binders. Preliminary results show that a polymer formed from tribromophenoxyethyl methacrylate (TBPOEMA) is as efficient a flame retardant as P(DBPA). Unfortunately the P(TBPOEMA) was available from Dow Chemical Company only as a powder at the time the experiments were performed. Since a good emulsion could not be made from this powder, this finish could not be adequately evaluated. As soon as the P(TBPOEMA) becomes available as a latex from emulsion polymerization, it should be subjected to more thorough characterization in these applications.

FLAME RETARDANT SYSTEMS BASED ON COMBINATIONS OF PHOSPHORUS AND BROMINE

1. Optimization of Phosphorus-bromine Formulations

Once a sufficient understanding of the action of phosphorus and bromine had been established, a series of experiments were undertaken to determine on a more quantitative basis the effects and interactions of phosphorus and bromine retardants when they are used together. One system meeting this requirement is tris(dibromopropyl) phosphate (TBPP). Because of durability considerations, this is not a practical candidate for commercial treatment of blends but it should be an instructive model for the study of this particular approach. For this reason, a series of blend fabrics was impregnated with varying levels of TBPP and their thermal properties studied. In an effort to determine the effect of the distribution of the flame retardant among the two fibers, a series of fabrics was padded with the retardant and heat treated to 150°C. Half of them were then washed in acetone to remove as much of the TBPP as possible from the cotton portion of the blend. Oxygen index values were found to reflect only the amount of retardant present in the sample and not the method by which level was achieved. This would indicate only minimal dependence of flammability on flame retardant distribution.

Since it would also seem to be important to determine the relative contribution of the two atomic species to the flame retardant action of TBPP, triallylphosphate was prepared as a model containing only phosphorus. The triallylphosphate was applied to samples of 65/35 and 50/50 polyester/cotton blends at levels ranging from 10% to 30% add-on. This would give a range of phosphorus from approximately 1% to 4%. The OI values of these fabrics were found to increase slowly with increasing phosphorus content up to about 2% phosphorus, beyond which the added phosphorus had essentially no effect on OI values.

In an effort to more completely characterize the bromine-phosphorus system, experiments were carried out utilizing variable

Br/P ratios.

In this work diammonium phosphate (DAP) was used as the model phosphorus compound and tris(dibromopropyl) phosphate (TBPP) as the model bromine compound. Bromine and phosphorus contents of the treated samples, together with heat release data are shown in Table XCI. Heat release values are also shown in Figure 98, plotted as a function of phosphorus content. It appears that data from all three treatments fall on the same curve, with slight variation in the values from that treatment in which the order of adding the retardants was reversed. This is probably due to a difference in TBPP content. As shown in Table XCI, bromine contents of these samples vary from 7 to 8%. Because of the variations in bromine content, $-\Delta H_1$ of the control was not used in the calculation of the net heat reduction, $\Delta H_1 - (\Delta H_1)_{\text{control}}$. Instead, $(\Delta H_1)_{\text{control}}$ was calculated from the efficiency equation (Table XCI) for TBPP for each sample as shown in Column 4 of Table XCI, and net heat reduction of each sample was obtained as the difference of the heat release, ΔH_1 , and the calculated $(\Delta H_1)_{\text{control}}$. The plot of net heat reduction vs. %P is shown in Figure 99. Values from all three treatments are on the same curve, indicating that the order of treatment in this binary system does not seem to affect the efficiency of either retardant. Values of heat reduction from 50/50 blend treated with DAP alone are included in Figure 99. There is a consistent difference of about 70 cal between the two curves, with the single treatment of DAP having the lower values. However, the standard experimental error estimated for ΔH_1 is $\pm 5\%$, or about 70 cal for these samples, the difference observed is not significant enough to warrant an argument of synergistic effects in DAP/TBPP systems.

Since the order of treatment is apparently not important in determining the efficiency of this system, it should be possible to predict the effect of any particular formulation from the characteristics of each component alone. Experimental confirmation of this is shown in Figure 100. The efficiency curves produced by adding DAP to the fabric have the same shape regardless of whether addition is made to a fabric containing 0% or 7% Br. Similarly the curves produced by adding T23P are parallel starting at 0% and 1%P. Thus one can use

TABLE XCI
CALORIMETRIC DATA OF 50/50 BLEND TREATED WITH DAP/TBPP
(WITH FIXED TBPP)

<u>% Br</u>	<u>% P</u>	<u>$-\Delta H_1, \frac{\text{cal}}{\text{gm}}$</u>	<u>$-(\Delta H_1)_{\text{Calc.}^*} \frac{\text{cal}}{\text{gm}}$</u>	<u>$\Delta H_1 - (\Delta H_1)_{\text{Control}}, \frac{\text{cal}}{\text{gm}}$</u>
1st. Treatment				
7.04	0.16	1876	2291	415
7.36	0.35	1641	2261	620
7.70	0.64	1487	2229	742
7.76	0.89	1462	2223	761
2nd. Treatment				
7.36	----	2255	2261	6
7.55	0.86	1398	2243	845
8.11	1.38	1356	2191	835
7.39	2.03	1277	2258	981
7.27	2.26	1228	2269	1041
Reversed Treatment ⁽¹⁾				
7.56	0.54	1467	2242	775
7.40	0.95	1415	2257	842
7.07	1.27	1359	2288	929
6.85	1.73	1360	2309	949

*Calculated from the % Br and the regression equation for the efficiency of TBPP; $\Delta H_1 - (\Delta H_1)_{\text{control}} = -7 + 93.5 (\% \text{ Br})$ and $-\Delta H_1$ of the untreated control.

¹Order of treatment reversed; TBPP first, the DAP.

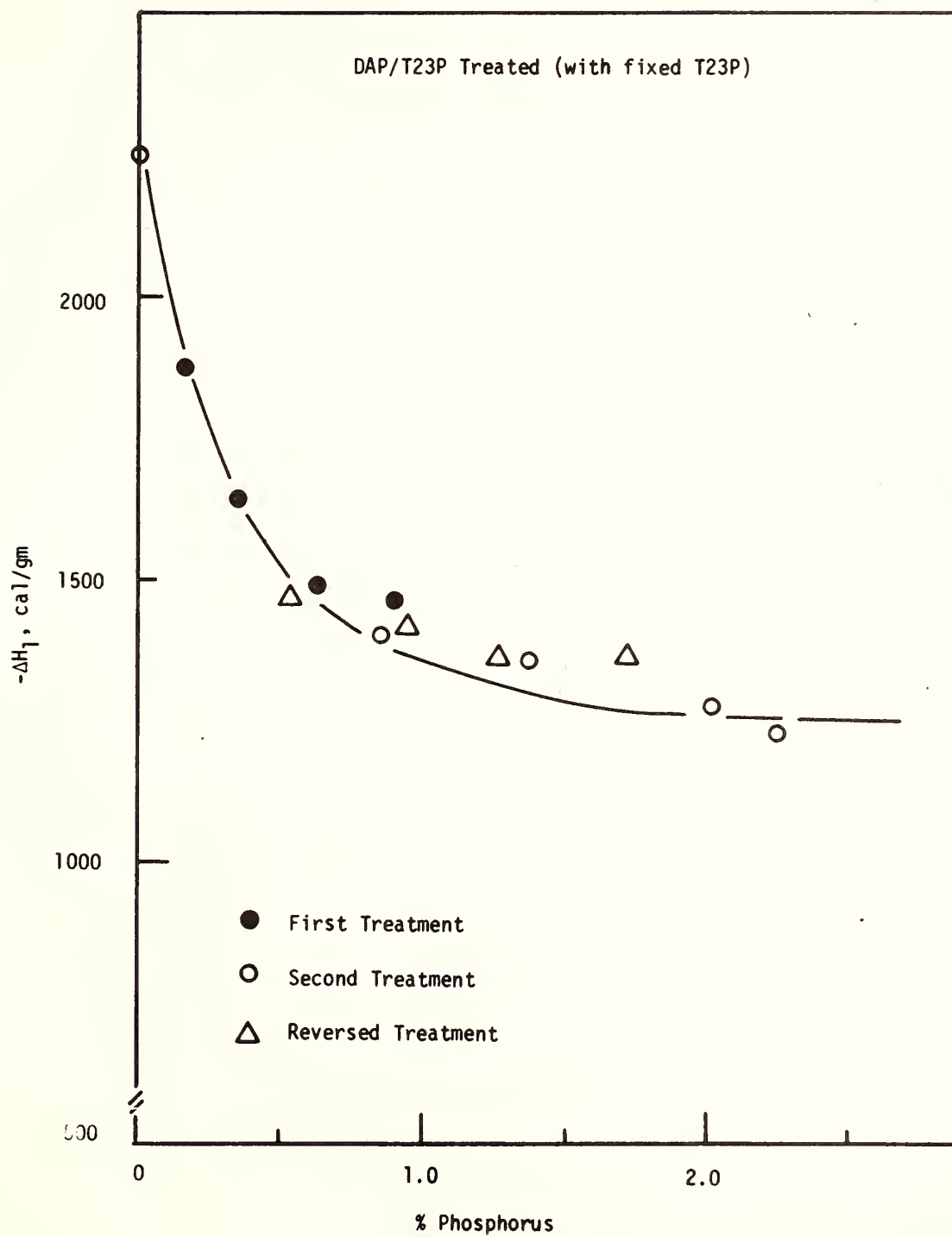


FIGURE 98. Heat release from DAP/T23P treated blend fabric with constant T23P content.

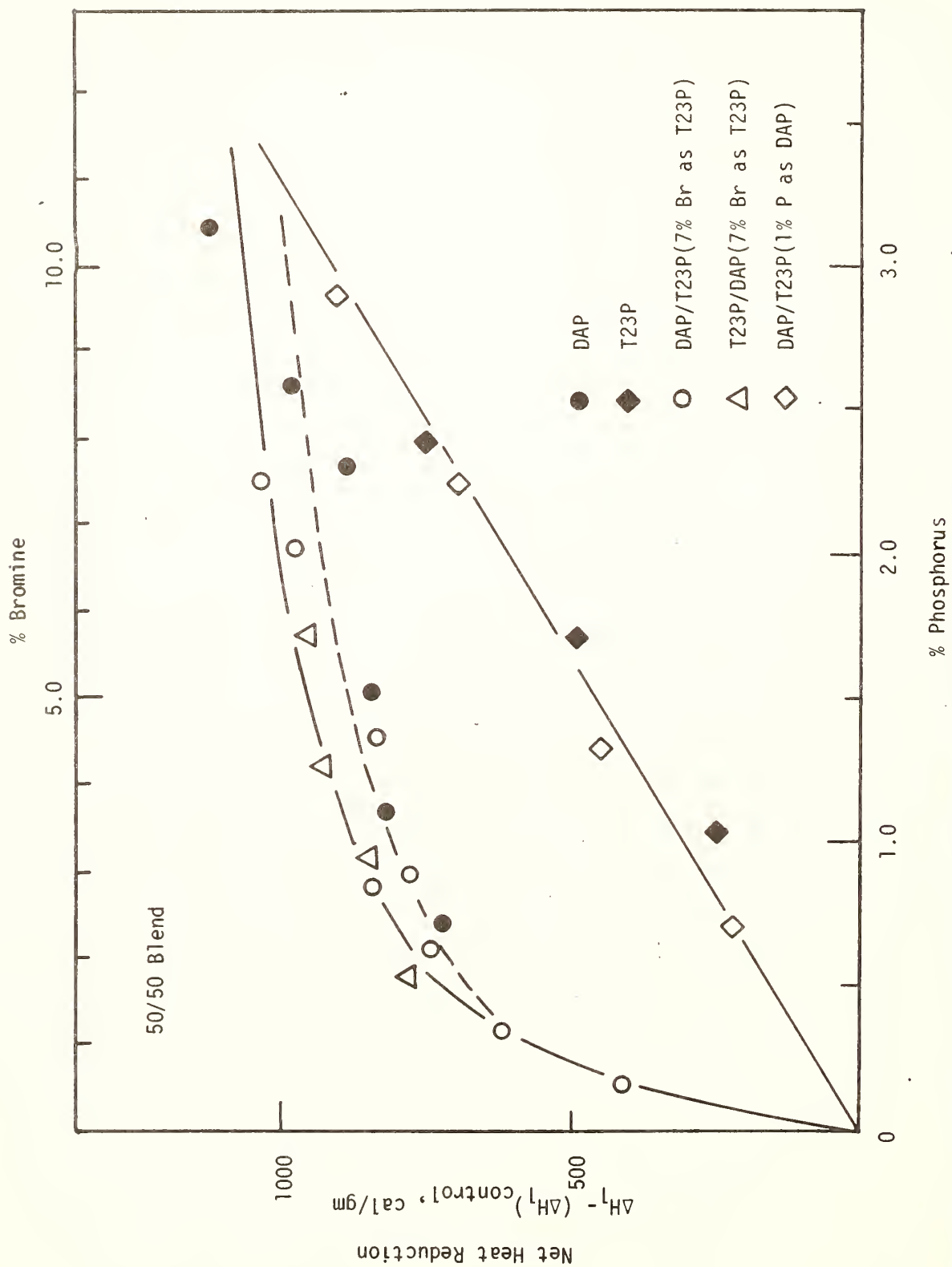


FIGURE 99. Net heat release of DAP/T23P treated 50/50 blends.

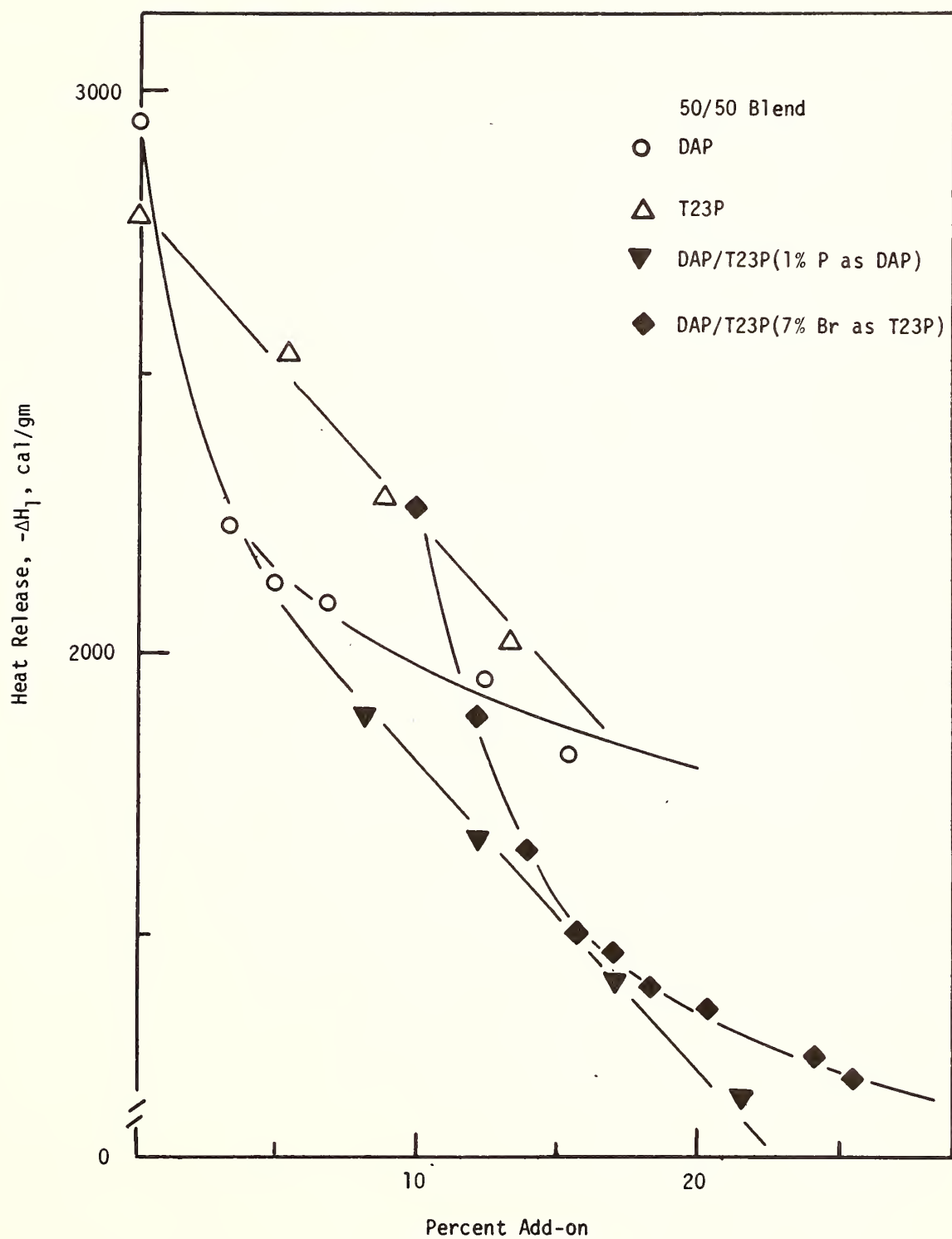


FIGURE 100. Calorimetric data for optimization of P/Br finishes.

these curves to arrive at those formulations of DAP and T23P which will produce a given heat release. To do this one need only select a point on the DAP curve corresponding to a specific P content, from this point draw a line parallel to the T23P curve, and proceed down this curve to a point corresponding to the desired heat release. The amount of Br required can then be read directly from the abscissa.

Whether this is a general approach which would be valid for other P/Br retardant systems remains to be determined experimentally. However, if it should be found to be valid, it should constitute a powerful tool for the optimization of formulations for characteristics not related to flammability such as cost, hand, ease of application, etc.

2. Interaction of Flame Retardant Fibers

Studies were also conducted to determine the ways in which both untreated and flame resistant polyesters interact with cellulosic fibers in a blend environment. Evaluation of flammability behavior was carried out both by oxygen index and by visual examination of a subjective nature while the materials were burned at a 45° angle on a pin-frame. Those systems containing phosphorus based flame retardants in the cellulosic portion were generally quite difficult to ignite. Correlation of these results with the results obtained using the isoperibol calorimeter indicate that as a general rule, the ignition of cotton/polyester blend fabrics is controlled to a great extent by the ease of ignition of the cellulosic portion. Those materials in which the cellulose is effectively rendered flame resistant show greater resistance to ignition. Once ignited, the flammability characteristics of the blends seemed to be controlled by the polyester portion. Another general observation made during the subjective burning test was the effect of burning off of volatile flame retardant before ignition of the substrate. This was especially prevalent in studies in which various samples had been treated with volatile organo-bromine systems. Even samples with an oxygen index as high as 27 would burn once substrate ignition was effected. This typically required approximately 20-seconds with a paper match.

Previous work had indicated that calorimetric techniques provided one of the best probes in the flammability behavior of such systems. In an attempt to provide support for the empirical experimentation and to provide information necessary for the design of new flame retardant systems, calorimetric investigations were initiated to determine some of the basic parameters relating to the flammability of treated cotton/polyester blend fabrics. These involved the use of both static oxygen bomb and isoperibol calorimetry techniques. Because many of the samples involved in these studies produced large amounts of smoke and particulate matter, it was necessary to develop new isoperibol calorimeter designs which would allow easy access to the internal parts of the calorimeter for cleaning. This was necessary in order to maintain

constant heat exchange characteristics. Calorimeters were thus built and calibrated and in order to form a basis for comparison with previous isoperibol calorimetric studies, a series of cotton/polyester blends of similar construction and weight, ranging in composition from 100% cotton to 80/20 polyester/cotton was re-examined. Results of this investigation are shown in Table XCII. The residue yields from both sets of measurements are essentially identical. The heat values are slightly, but consistently, higher in the more recent measurements. Both sets of heat data are plotted versus cotton content in Figure 101. The shape of both curves is essentially the same with a minimum at approximately 55% cotton. The maximum deviation between the two curves is approximately 150 calories. This difference could be due to slight quenching at the top of the earlier calorimeter. This should have been reduced in the later design.

The rates of heat release are plotted as a function of the cotton content in Figure 102. The rates from both measurements are the same for the cotton rich blends, but the data obtained on the new calorimeter tend to deviate from the previous data in the area of the polyester rich blends. Both sets of rate data show linear relationships when plotted as a function of cotton content.

The effect of adding flame retardants selectively to either the cotton or polyester portions of the blend was then studied.

Four fabric samples listed below were obtained from FMC Corporation. Additional fabric samples shown below were obtained from the Fibers Division of DuPont.

- 50/50 PET/HWM Rayon
- 25/75 PET/PFR Rayon
- 50/50 PET/PFR Rayon
- 35/65 900F/PFR Rayon
- 50/50 900F/Cotton
- 65/35 900F/Cotton

The calorimetric results from these blends are shown in Table XCIII. The 50/50 polyester/high wet modulus rayon gave very high residue yield (40%) and a low heat value when burned without support. This

TABLE XCII

CALORIMETRIC DATA OF POLYESTER/COTTON BLENDS -- COMPARISON OF CALORIMETERS

% Cotton	% R ⁽¹⁾		-ΔH ₁ , cal/gm ⁽²⁾		Rate, cal/gm-sec ⁽³⁾	
	Mark IV	Mark II	Mark IV	Mark II	Mark IV	Mark II
100	---	---	3334	3334	79.9 ±	78.7 ± 1.0
87.5	---	---	---	3047	----	75.6 ± 1.0
75	---	---	2926	2761	71.6 ± 1.8	73.6 ± 1.0
62.5	5.5	3.3	2755	2606	66.0 ± 0.9	71.9 ± 2.0
50	6.6	5.2	2767	2627	62.0 ± 1.8	69.1 ± 3.3
35	8.7	4.6	2846 ⁽⁴⁾	2776	54.2 ± 0.4	69.5 ± 2.4
20	7.6	6.6	3183 ⁽⁵⁾	3173	45.4 ± 1.3	65.6 ± 3.0

¹All results reported are averages of at least three runs²Standard deviation = ±3% from calibration³Rate obtained from sample 5.1 cm wide and 12.7 cm long⁴Supported with three metal wire stitches⁵Supported with fiber glass gauze

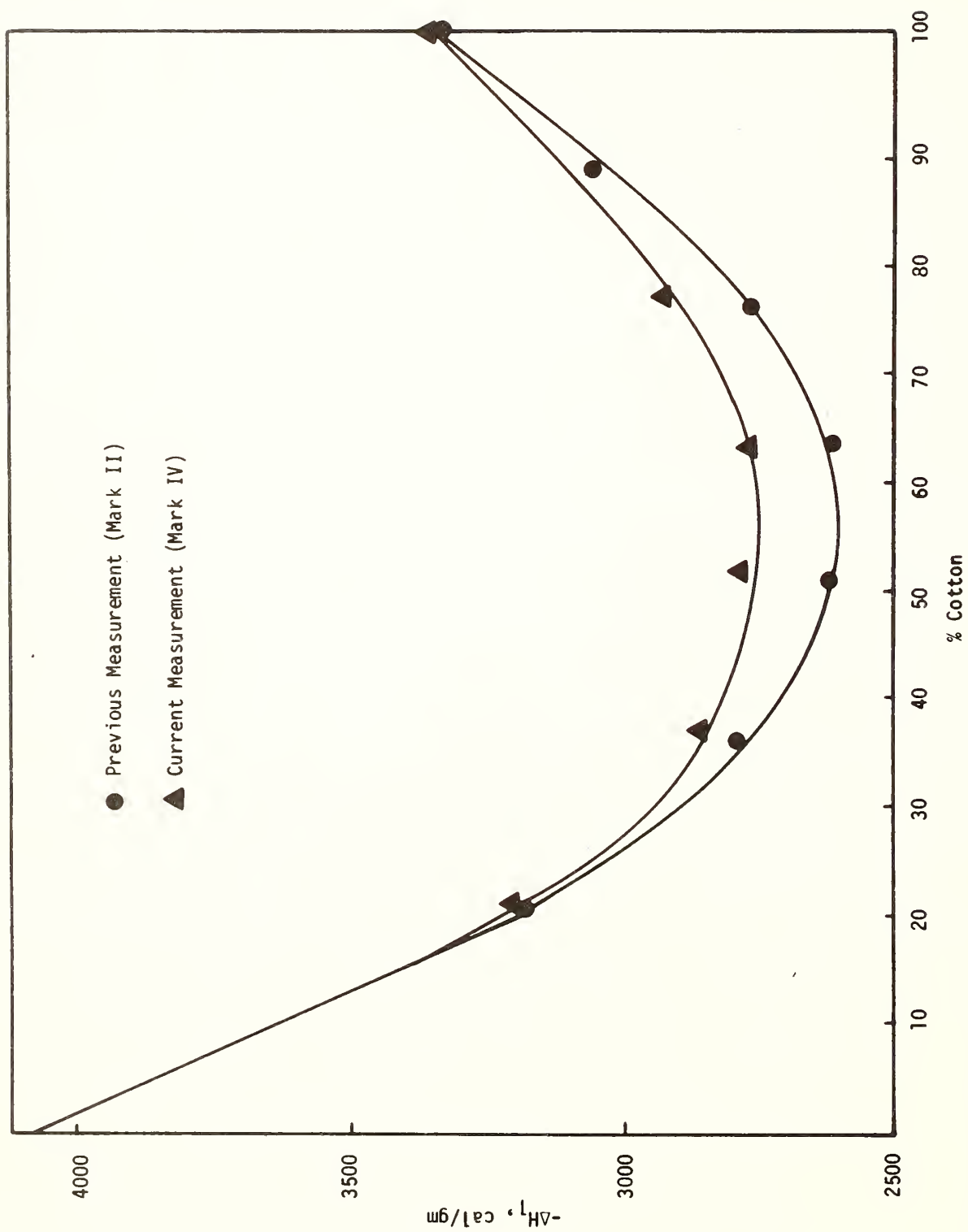


FIGURE 101 Effect of fiberglass grid on ΔH_f of PET/cotton blends.

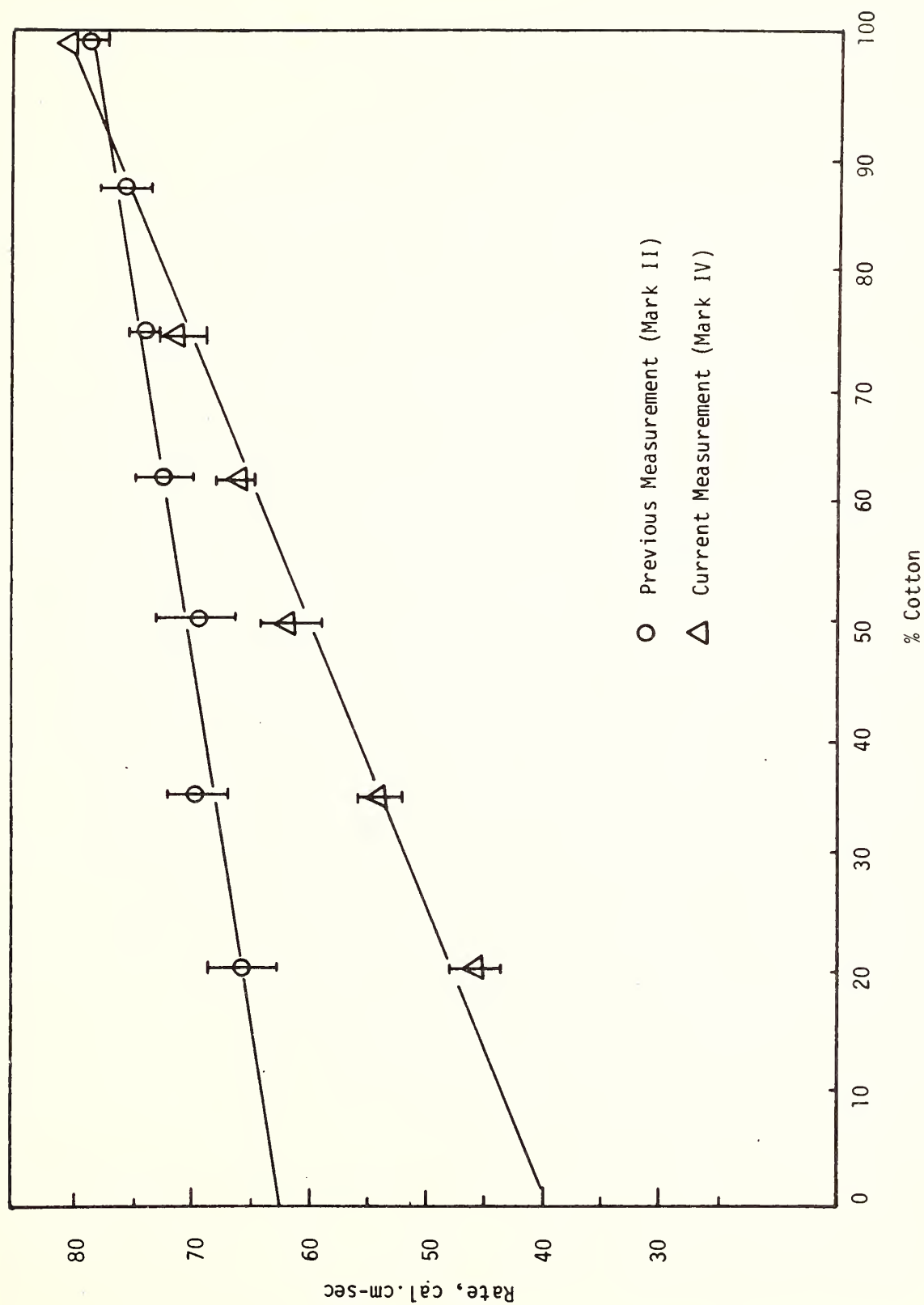


FIGURE 102. Rates of heat release of PET/cotton blends.

TABLE XCIII
CALORIMETRIC DATA OF SOME EXPERIMENTAL POLYESTER/CELLULOSE BLENDS⁽¹⁾

Blend	% Residue	$-\Delta H$, cal/gm ⁽²⁾	Rate, cal/cm-sec ⁽³⁾
50/50 PET/HWM Rayon	39.9	1436	50.5 \pm 1.7
	4.1 ⁽⁴⁾	3055 ⁽⁴⁾	46.3 \pm 0.4 ⁽⁴⁾
25/75 PET/PFR	22.4	2245	60.9 \pm 3.4
50/50 PET/PFR Rayon	15.1	2256	52.7 \pm 3.0
35/65 900F/PFR Rayon	21.2	1936	44.8 \pm 1.7
50/50 900F/Cotton	4.6	2809	43.7 \pm 0.9
65/35 900F/Cotton	10.8	2443	44.2 \pm 2.1

¹All results reported are averages of at least three runs

²S. D. = $\pm 3.0\%$ (estimated from calibration)

³Rate obtained from sample 5.1 cm wide and 12.7 cm long

⁴Supported with fiber glass gauze

appeared to be due to excessive melting and dripping which was completely unexpected since similar blends of polyester and cotton scarcely melt or drip during burning. However, when the polyester/rayon blend was burned with a fiber glass gauze support, the residue yield decreased by 10-fold and heat evolution more than doubled. The rate of heat release data from this blend obtained on both supported and unsupported burning may be misleading since the rate is dependent upon the width of the specimen, or the width of the flame. Excessive melting and dripping would completely distort the shape of the specimen; thus no uniform width of flame front could be expected throughout the burning.

The two polyester/PFR rayon blends gave almost identical amounts of heat when burned. Residue yield was much higher for the 25/75 blend than for the 50/50, as expected, since the char comes essentially from the cellulosic component. However, the exact levels of retardant incorporated in these two blends is not known and further comparison of the results is meaningless at the present time. The blend of the 900F polyester with PFR rayon seems to be the most promising of this series.

The availability of Dacron[®] 900F as a flame retardant polyester has also led to its use in studying the effect of adding specific retardants to the cotton portion of a flame resistant blend.

Blends using Dacron[®] type 900F aftertreated with diammonium phosphate produced good flame resistance with good aesthetic and physical properties at relatively low add-on. These data suggested an approach consisting of a very efficient treatment on the cellulose combined with an inherently flame retardant polyester, such as Dacron[®] 900F. Based on this observation, an attempt was made to treat a 50/50 blend of cotton and Dacron[®] type 900F with the Monsanto MCC100/200/300[®] finish. Under the conditions employed, only a low level of flame retardant add-on was achieved, and thus there was no significant improvement in the flame retardant characteristics of the blend. Further experiments in this vein should be fruitful but were discontinued in this work because of the lack of a source of supply for large quantities of the blend fabric.

Instead efforts were concentrated on attempts to elucidate the basic characteristics of Dacron[®] 900F in blends with cotton. Three fabrics of 50/50 blends and three of 65/35 of different weights and constructions were obtained from DuPont, along with 50/50 and 75/25 experimental 900F/cotton blends containing higher bromine contents. The results of the isoperibol calorimetric studies on the six blends containing the regular type 900F are shown in Table XCIV. These data seem to confirm that physical properties, such as fabric weight and construction, do not significantly affect results of the calorimetric studies. A similar effect was observed recently on a series of 100% cotton fabrics. This points out one of the important characteristics of the isoperibol calorimetric technique which enables it to effectively detect and evaluate chemical flame retardants on specific fibers in a variety of fabric types.

Results from two of the regular 900F/cotton blends, one a 65/35 and one a 50/50 blend, show that the untreated material yielded slight increases in char formation and noticeable decreases in heat evolution as the contents of 900F in the fabrics increased. On this basis it was determined that these blends should have potential for effective after-treatment using systems capable of exerting condensed phase flame retardant activity on the cellulosic portion. These fabrics were therefore treated with phosphoric acid as a model system at varying levels of add-on ranging from 1½%-6% (0.5%-2.0% P). The treated blends were then studied by isoperibol calorimetry and the results tabulated in Tables XCV and XCVI.

The char yields obtained with these blends are compared with those obtained from normal polyester/cotton blends in Table XCVI. The expected char yields from the cotton portion of the blends were calculated from previous data on phosphoric acid treated 100% cotton fabrics and are included in Table XCVI for comparison. The 50/50 900F/cotton blend produced char yields which were essentially the same as those calculated on the basis of the cotton content up to about 1½% phosphorus. However, the char yield from the fabric containing 1.9% phosphorus was more than double that expected on the basis of char formation from the

TABLE XCIV

ISPERIBOL DATA OF 900F[®]/COTTON BLENDS WITH VARIOUS FABRIC WEIGHT AND CONSTRUCTION

Fabric	Fabric wt. oz/yd ²	Construction	%R	Rate, cal/cm-sec	-ΔH _f , cal/gm
50/50 900F [®] /Cotton	2.8	woven	5.6	49.0	2739
	3.8	woven	4.1	57.5	2637
	5.0	knit	3.7	51.9	2771
			4.5 ±1.0	52.8 ±4.3	2716 ±70
65/35 900F [®] /Cotton	3.8	woven	10.5	48.0	2401
	4.2	woven	9.6	49.0	2409
	5.0	knit	9.8	43.4	2436
			10.0 ±0.5	47.1 ±3.2	2415 ±18

TABLE XCV
ISOPERIBOL DATA OF H_3PO_4 TREATED 900F^(R) COTTON BLENDS

Samples	%P	%R	Rate, cal/cm-sec	$-\Delta H_1$, cal/gm
50/50 900F ^(R) / control		4.6 \pm 0.3	43.7 \pm 0.9	2809
Cotton	0.58	15.7 \pm 0.6	38.8 \pm 2.6	2001
	1.43	23.4 \pm 5.2	24.4 \pm 6.1	1658
	1.90	55.1 \pm 0.2	21.3 \pm 0.5	1066
65/35 900F ^(R) / control		10.8 \pm 2.0	44.2 \pm 2.0	2443
Cotton	0.65	15.9 \pm 0.3	32.7 \pm 2.6	1524
	1.20	23.5 \pm 2.0	15.2 \pm 2.6	1441
	1.57*	26.2	17.3	1303
	1.83*	40.1	11.2	1162

*Only one specimen run.

TABLE XCVI

CHAR YIELDS OF H_3PO_4 TREATED 900F^(R)/COTTON AND POLYESTER/COTTON BLENDS

Sample	%P	%P cotton ⁽¹⁾	%R		calc. ⁽²⁾
			900F ^(R) /cotton	PET/cotton	
50/50 blend	control	--	4.6	5.2	5.2
	0.58	1.16	15.7	14.6	16.0
	1.43	2.86	23.4	19.8	23.7
	1.90	3.80	55.1	21.6	26.0
65/35 blend	control	--	10.8	8.7	8.7
	0.65	1.86	15.9	13.6	14.0
	1.20	3.43	23.5	16.6	17.6
	1.57	4.49	26.2	17.8	19.3
	1.83	5.22	40.1	18.5	20.1

¹%P content based on mass of cotton in the blend

²Calculated from previous data on H_3PO_4 treated 100% cotton using %P cotton

cotton portion only. Similar behavior was noted for the 65/35 900F/cotton blends. These fabrics gave slightly higher char yields than those calculated on the basis of the cotton portion. However, the largest difference again occurred at about 1.8% phosphorus content where the 900F/cotton blend gave twice the amount of char calculated on the basis of cotton content. Both blends (50/50 and 65/35) became very difficult to ignite at their highest level of treatment. On the basis of subjective observations of the burning characteristics in the calorimeter, it is estimated that a phosphorus content of 2.0% should be sufficient to effectively inhibit burning and that these fabrics should pass FF 3-71.

The flame retardant contribution of the bromine in the 900F Dacron[®] is probably due to a vapor phase mechanism and is not significantly related to char formation. At the lower levels of add-on (up to 1.5% phosphorus for 50/50 and 1.0% for 65/35) where there is still sufficient heat generation from the cotton portion of the blend to sustain the combustion process, there is essentially no residue from the polyester remaining in the char. However, at higher phosphorus contents, (1.8% to 1.9%) the diminished heat generation from the cotton portion coupled with the probably vapor phase retardance from the 900F results in a large reduction in total heat generation and thus in the heat fed back to the substrate. This apparently results in a decrease of the heat flux at the fabric surface to a point where it is not sufficient to sustain complete degradation of either the cotton or the polyester. Therefore, a large quantity of residue is left.

The dependence of the heat release for both the 900F/cotton blends and the normal PET/cotton blends is presented graphically in Figure 103. The 50/50 blends exhibit heat release values which are essentially the same for the two blends up to about 0.5% phosphorus. At higher phosphoric acid add-ons, the heat release from the PET/Cotton blend remained unchanged. A similar behavior was observed with the 65/35 blend, although the heat release of the untreated system containing 900F was about 400 calories lower than that containing the normal polyester, indicating the effect of the bromine in the 900F. Similarly the heat release from the untreated 65/35 blend containing 900F was

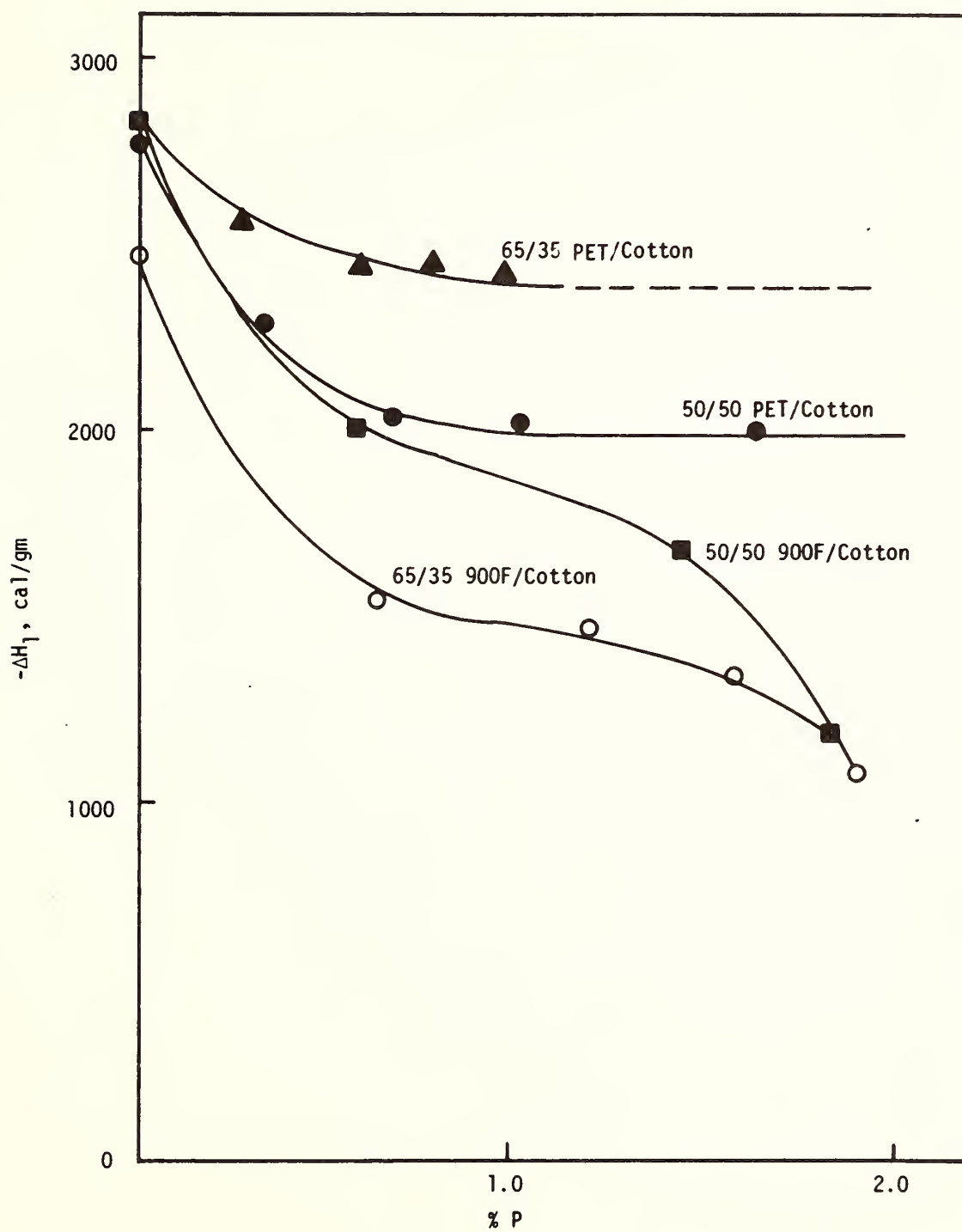


FIGURE 103. Heat release of H_3PO_4 treated 900F/cotton blends.

also about 400 calories lower than that of the 50/50 900F cotton blends. This is presumably due to the larger amount of bromine in the 65/35 blend.

The effect of the bromine can be seen more clearly if the heat release (ΔH_1) is shown as the sum of the heat release from the cotton and the polyester portions of the blend as follows:

$$\Delta H_1 = Q_c + Q_p \quad \{9\}$$

where Q_c and Q_p are respectively the heat release from the cotton and polyester portions of the blend. If one assumes that the combustion of cotton in the blend is the same as that in the form of 100% cotton fabric, the Q_c can be calculated from the previous data obtained on 100% cotton treated with phosphoric acid, and Q_p can be calculated from equation {9}. The plots of ΔH_1 , Q_c , and Q_p as a function of percent phosphorus are shown in Figure 104 for the 50/50 blends, and in Figure 105 for the 65/35 blends. Both Figures 104 and 105 show the drastic difference in heat release from the 900F and the regular polyester. For either blend, as Q_c decreases with increasing phosphoric acid content, Q_p increases, while the total heat (ΔH_1) remains essentially constant. However, Q_p in the case of 900F remains unchanged until the phosphoric acid content is increased to about 1.5% phosphorus. It then drops drastically to below 1000 calories at 1.8%-1.9% phosphorus, while Q_c is less than 400 calories. These data indicate a distinct retardant effect as compared with those of the regular polyester. The heat release values are in agreement with the char yield data, and show that up to 1.5% phosphorus the heat release from 900F is essentially unaffected by the presence of the phosphoric acid. Such results were expected since phosphoric acid is a condensed phase retardant and has no known retardant effect on polyester. The drastic retardant effect observed on 900F cotton blends at a phosphorus content above 1.5% is probably due to the synergistic effect which results from the reduction in heat release from the cotton portion and vapor phase retardant effect from the bromine. This should produce an insufficient heat feedback to the substrate, resulting in less than complete degradation of both polymers. This, in turn, of course, reduces the amount of fuel gas available to the flame, and the effect is consider-

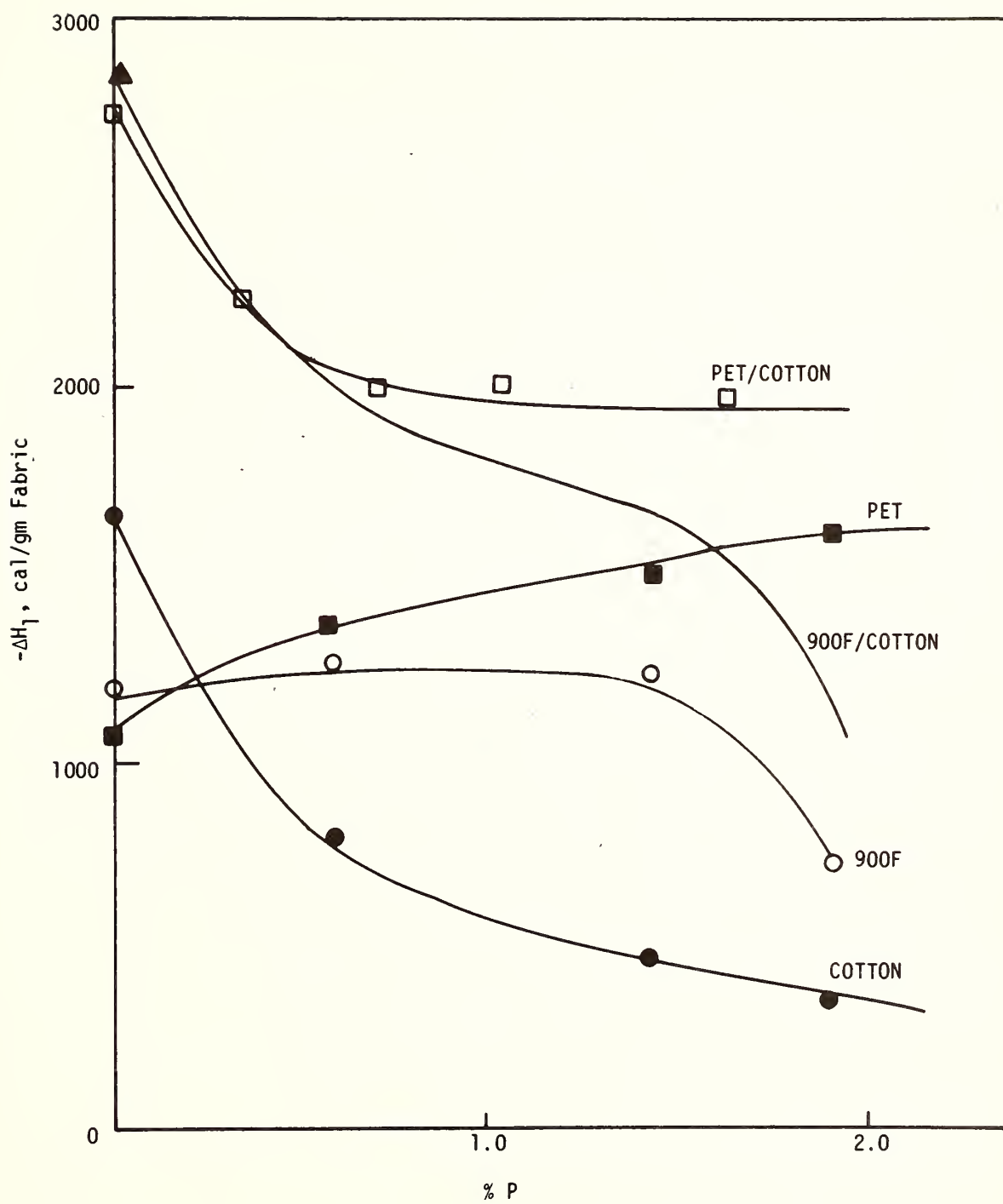


FIGURE 104. ΔH_1 of H_3PO_4 treated 900F/cotton and PET/cotton 50/50 blend fabrics.

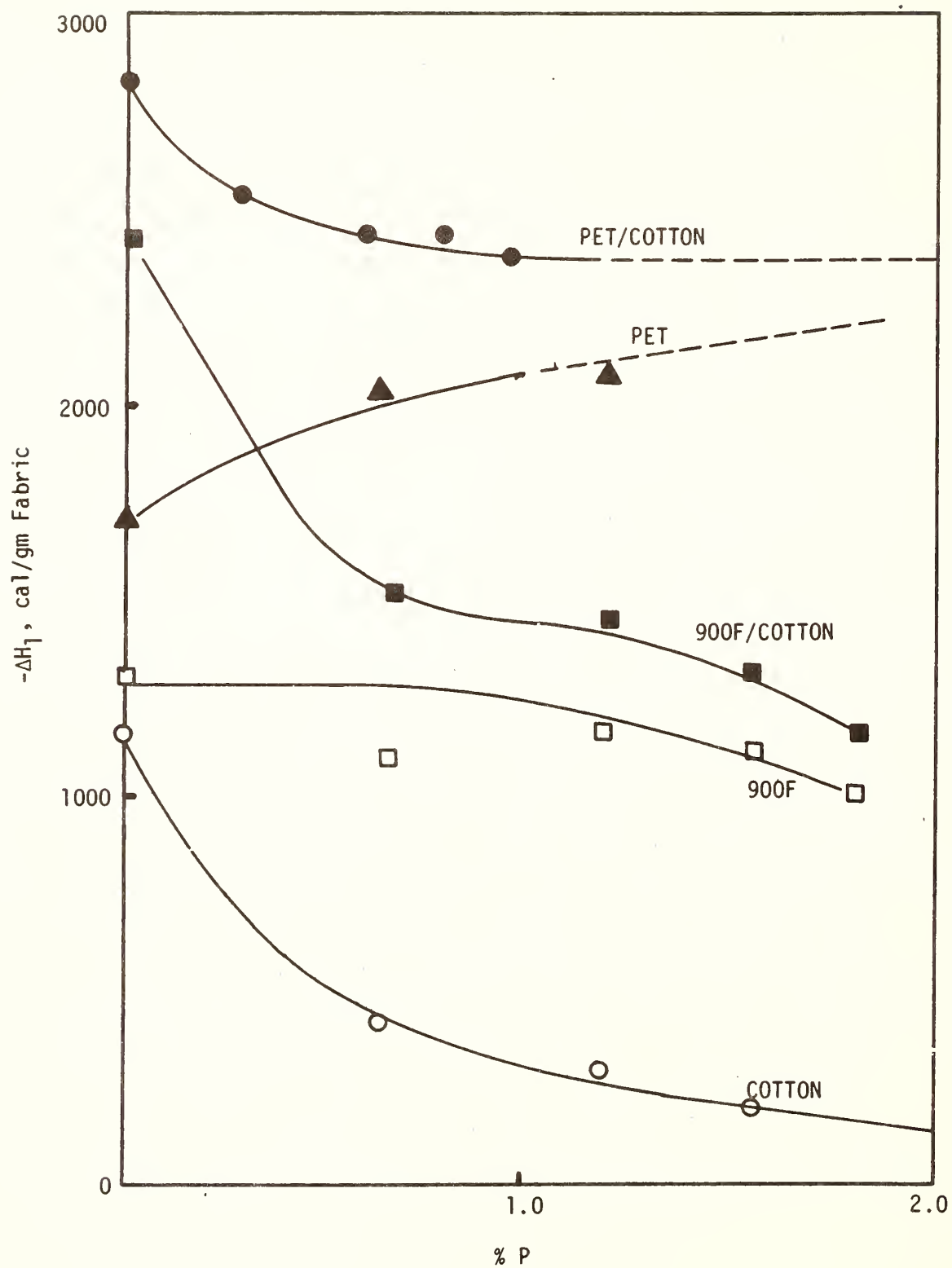


FIGURE 105. ΔH_1 of H_3PO_4 treated 65/35 900F/cotton and PET/cotton blend fabrics.

ably greater than additive.

In an effort to further evaluate the flame retardant action of the bromine, experimental samples of 900F containing 7.5% bromine instead of the normal 6.0% were obtained from DuPont in the form of 50/50 and 75/25 blends with cotton. These two fabrics were also treated with phosphoric acid at three different levels of add-on up to 1.8% phosphorus. The isoperibol results on these blends in treated and untreated forms are shown in Table XCVII, together with similar samples based on the normal 900F fiber. Heat release values were also plotted as a function of %P and are shown in Figure 106. These four series of blends contain different levels of bromine, ranging from 3.0 to 5.6 due to the different ratios of 900F and cotton. Figure 106 shows that blends with higher bromine content tend to release less heat than the ones with the lower bromine content at the same phosphorus add-on. Two phosphoric acid treated 75/25 blends failed to burn in the calorimeter; these had phosphorus contents of 1.68% and 1.80%. However, the trend which shows decreasing heat release with increasing bromine content is clearly demonstrated. The significance of bromine in these blends can be shown if the heat release data is further reduced. Figure 107 shows a plot of heat release versus bromine content at several levels of phosphorus. This graph shows the linear decrease of ΔH_1 with increasing bromine content. Furthermore, since these data represent three different blends, the linear dependency of ΔH_1 on bromine content significantly demonstrates one of the important characteristics of vapor phase retardancy, i.e. the effectiveness of vapor phase retardants should be independent of the nature of the substrate. Values for the 65/35 blend are consistently off the line. This may be due to an error in the phosphorus content in the treated samples.

The fact that all of the lines in Figure 107 seem to parallel each other indicates that the effectiveness of the bromine on these blends is identical irrespective of the amount of phosphorus present in the blend. This tends to suggest that bromine and phosphorus are working independently of each other and is evidence that there is little or no bromine/phosphorus interaction or synergism such as has

TABLE XCVII
ISOPERIBOL DATA OF 900F^(R)/COTTON BLENDS WITH VARYING BROMINE CONTENT

Fabric	%Br	%P	%R	Rate, cal/cm-sec	-ΔH ₁ cal/gm
50/50 900F ^(R) /ct	3.0	control	4.6	43.7	2739
		0.58	15.7	38.8	2001
		1.43	23.4	24.4	1658
		1.90	55.1	21.3	1066
50/50 900F ^(R) /ct	3.8	control	7.2	52.7	2546
		0.47	17.7	35.1	1920
		1.28	21.9	23.2	1443
		1.67	35.5	20.1	1141
65/35 900F ^(R) /ct	3.9	control	10.8	44.2	2409
		0.65	15.9	32.7	1524
		1.20	23.5	15.2	1441
		1.57	26.2	17.3	1303
		1.83	40.1	11.2	1162
75/25 900F ^(R) /ct	5.6	control	11.1	39.3	2277
		0.72	21.0	15.5	1653
		1.28	37.6 ± 8.9*	----	1259 ± 208*
		1.68	did not burn		
		1.80	did not burn		

*Average of five runs, large error probably due to uneven treatment.

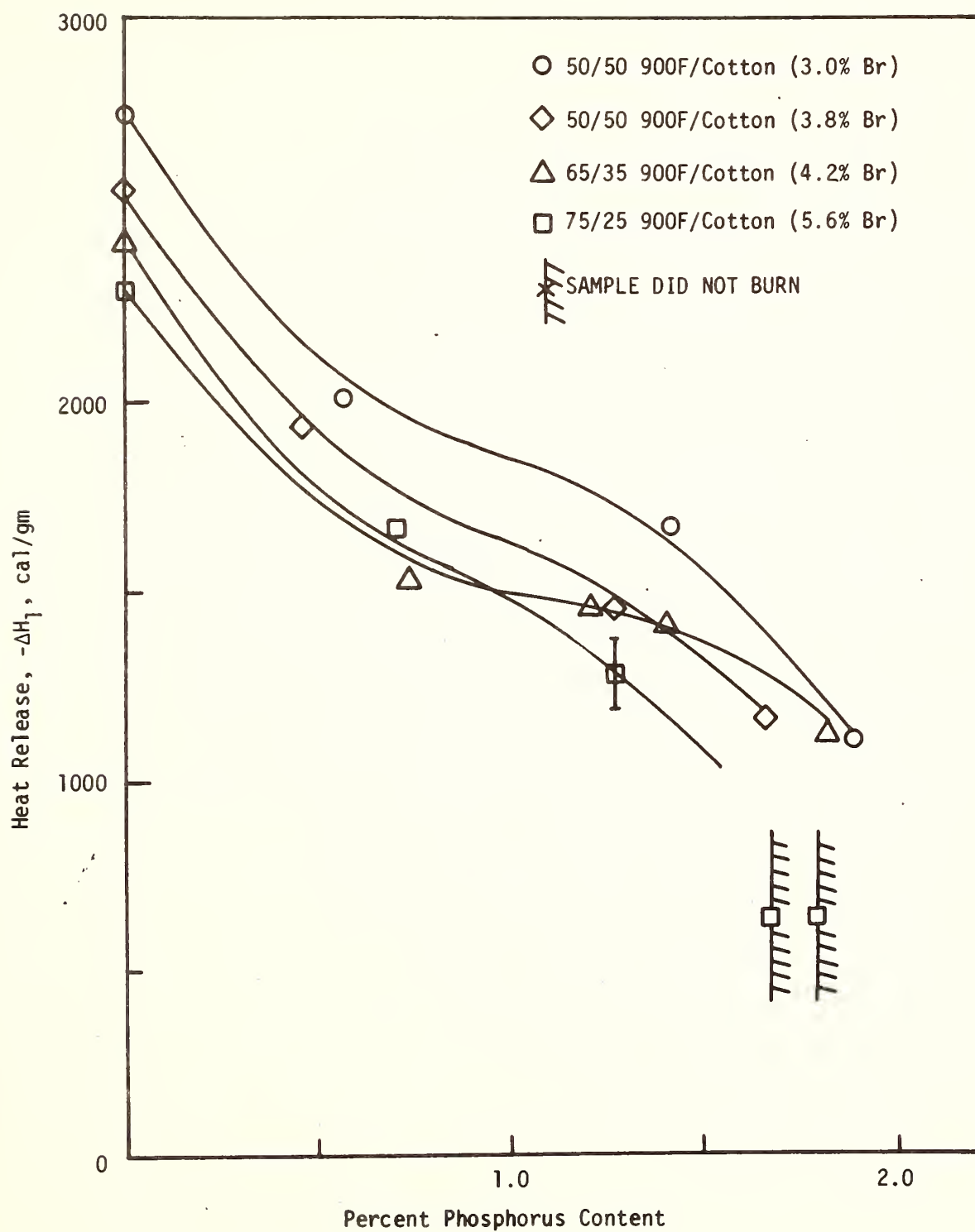


FIGURE 106. Heat release of various H_3PO_4 treated 900F/cotton blends.

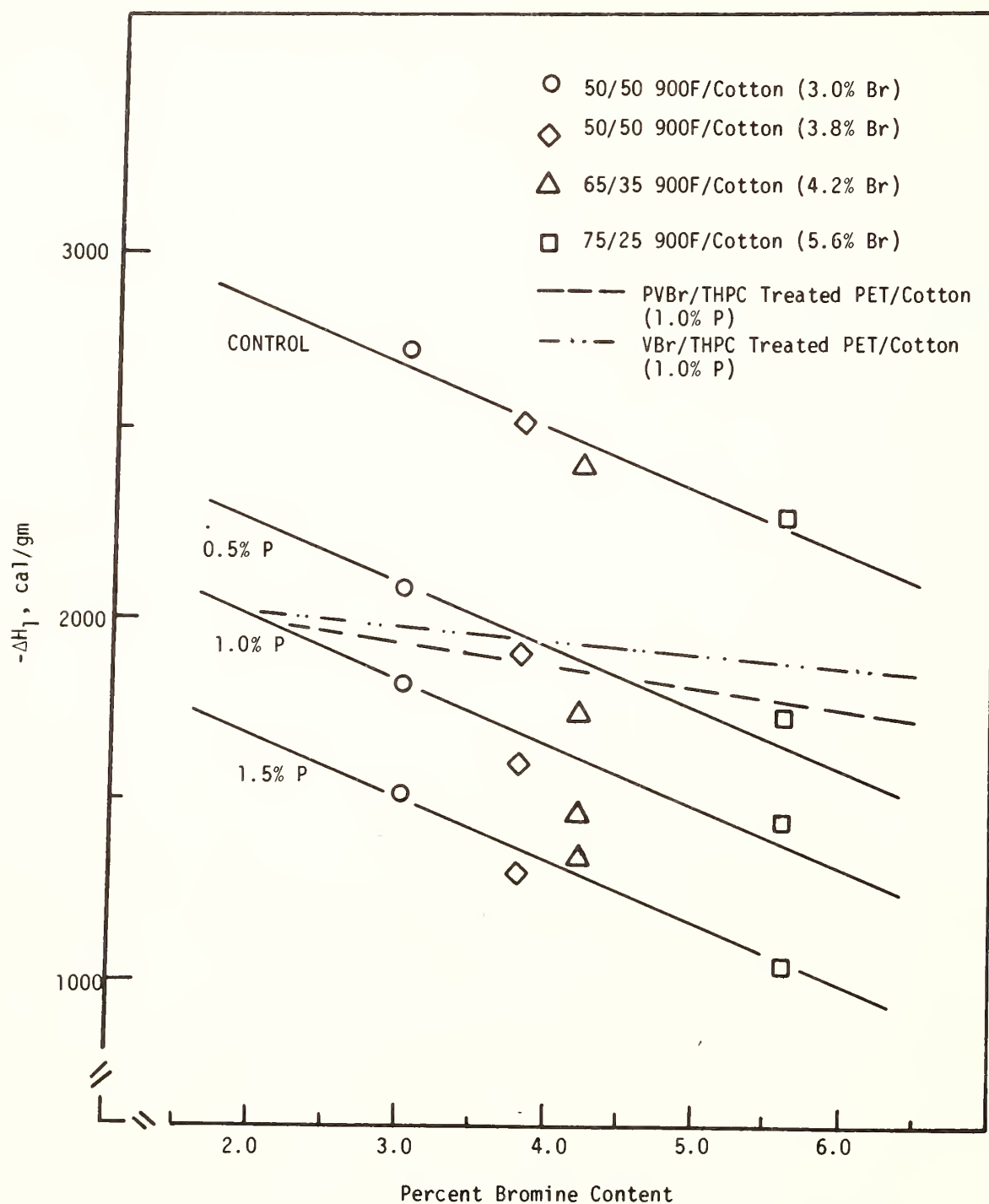


FIGURE 107. Heat release of various 900F/cotton and PET/cotton treated with H_3PO_4 or PBVr/THPC.

previously been suggested to exist in other systems.

3. Phosphorus/Bromine Systems Based on Phosphonium Salts

3.a. THPS[®]/urea/PVBr and related systems:

One of the first potentially commercial systems in which the action of both bromine and phosphorus was important was that based on the use of THPC/urea/polyvinylbromide as developed at SRRC under the direction of Mr. George L. Drake, Jr. several years ago. Because of the commercial potential of this system, considerable effort has been expended to attempt to modify the formulation to circumvent the problems of low reproducibility, color formation, and harsh hand which have been noted in several laboratories. Efforts were therefore undertaken by both Hooker Chemicals and Plastics Corporation, and SRRC to modify the application of the THPC portion of the system. At the same time, investigations were initiated at both Clemson University and the University of Maryland to further elucidate the chemical nature of the processes responsible for both the retardancy and the deleterious effects. Ethyl Corporation, the major producer of the polyvinylbromide used in this system, has actively participated and cooperated in these investigations. Ethyl Corporation provided samples of the polyvinylbromide in both pure and latex form, and also provided samples of selected copolymers of polyvinylbromide with other vinyl materials - particularly vinyl chloride. Initial investigations with these systems indicated some effect by both constituents, although the relative contributions could not be determined.

Studies conducted both at SRRC and Clemson demonstrated that the copolymers give much better performance during curing and produce only slight, if any, discoloration. Thus a program was undertaken at SRRC to further develop the THPC-urea-P(VBr/VCl) system. After considerable laboratory experimentation, the formulation given in Table CVIII was found to produce good results when applied in the SRRC pilot plant. Under these conditions a white fabric could be prepared having no discoloration, good flame resistance and good hand. It was also found that the hand of the samples produced using the standard ETIP 50/50

TABLE XCVIII

THPC/UREA/P(VBr/VC1) FINISH FORMULATION

	<u>% by weight</u>
THPC (80% aq.)	33.3
Urea	8.5
Na ₂ HPO ₄	4.0
NaOH (50% aq.)	3.0
P(VBr/VC1) emulsion (40%)	16.0
H ₂ O	35.0
Triton [®] 770	0.2

Procedure:

- 1) Dissolve Na₂HPO₄ in H₂O with stirring
- 2) Add THPC with stirring
- 3) Add Urea
- 4) Adjust pH to 6-6.5 with NaOH
- 5) Add P(VBr/VC1) emulsion
- 6) Add Triton[®] 770

Application:

Pad through above solution using ca. 6 tons pressure on squeeze rolls to get wet pick-up ca. 85%.

Dry 2 min at 85°C

Cure 1 min at 160°C

Wash in 1% H₂O₂ 2 min followed by 1 hot and 1 cold rinse

Dry

Fabric Analysis:

	<u>original</u>	<u>50X</u>
P	2.5%	---
Br	3.2%	---
Cl	1.5%	---
Char length (AATCC)	2.5 in	4.5 in

poplin could be further improved if the fabric was prescoured for 1½ hours using a warm scour bath containing 5% Mayquest® 80 (EDTA), 5% PreChem® SN (a halogenated aromatic), 5% PreChem® 70 (wetting agent) and 1% NaOH (all owf).

Because these results were so promising, a 250 yd. mill run was made at the Clearwater Finishing Plant of UM & M. This used the formulation that had been the best under the pilot plant conditions (Table XCVIII). After padding and drying for 58 sec. in a frame with three heating zones (reading 182°C, 202°C, and 152°C, respectively) the fabric was found to be insufficiently dried. It was therefore redried using the same temperatures with a residence time in the frame of 30 sec. The fabric was then cured for 2 min 15 sec at 154°C, washed 15 min in dilute Na₂CO₃, rinsed 5 min hot and 5 min cold, put through a scutcher and dried. The resulting fabric was very light purplish brown and somewhat stiffened. Presumably, at least part of this discoloration and stiffness was due to the extra drying that was required after padding.

Three polyvinylbromide lattices were applied to samples of 100% cotton, 100% polyester, and 50/50 cotton/polyester blend fabric. The three lattices were polyvinylbromide, a 50/50 copolymer of vinylbromide and vinylchloride, and a 94.7 to 5.3 copolymer of vinylbromide and N-methylolacrylamide. These lattices were applied in varying concentrations and the resulting OI's showed a linear relationship with the percent bromine present in the fabric. It was interesting that all three samples - cotton, polyester, and the blend - fell on the same line. It was also noticed that the chlorine in the polyvinylchloride portion of the copolymer seemed to have no significant effect on the oxygen index values exhibited by the samples.

A different set of samples was treated with the same polymer lattices but with a small amount of antimony oxide added to the pad bath. The addition of the antimony oxide resulted in an increase in the OI values on all the samples, with the largest effect being noticed on the polyester, and the smallest effect being noticed on the cotton. This would indicate that the antimony oxide was increasing the vapor phase

activity of the bromine present in the sample. The antimony oxide did not, however, increase the activity of the chlorine present, as again the chlorine and the polyvinylchloride did not affect the oxygen index observed for the samples.

Samples of both sets of treated fabrics were then burned on the 45° angle pin-frame and their burning characteristics subjectively evaluated. The antimony oxide had little effect on the manner in which the samples burned. All the samples burned with a thick grey smoke which seemed to result from the flame retardant itself burning off the surface of the fabric. The blend fabrics as well as the cotton fabrics would burn the entire length of the specimen leaving a substantial char which would then be consumed by an afterglow. The cotton samples from both treatments had an oxygen index of 26 but would not burn in the subjective evaluation. The blend fabrics and the polyester fabrics had similar OI values at the same bromine add-on, but they were observed to burn readily. This probably resulted because the cotton flame was not hot enough to burn off the flame retardant polyvinylbromide latex. The flame of the blend fabric, however, was hot enough to burn off the flame retardant and the fabric would, therefore, burn.

In another series of experiments, twenty (20) polyester/cotton blend fabric samples were prepared by Ethyl Corporation. These were first treated with THPC to a level of 1.0%P and then over-treated with polyvinylbromide (PVBr) or poly(vinylbromide/vinylchloride){P(VBr/VC1)} copolymer at various levels of add-on. Twelve of these fabrics, including a control, were selected for study by isoperibol calorimetry. The results of this study are given in Table XCIX. Two additional fabrics, one a 65/35 polyester/cotton blend, and the other a 50/50 polyester/rayon blend, treated with the THPC and PVBr at SRRC were also included in the study. The SRRC 65/35 polyester/cotton gave a lower char yield, a higher heat release, and a higher rate of heat release than the 50/50 blend, due mainly to the higher polyester content. Even though both blends were overtreated with THPC, a 3% bromine content was shown to be insufficient to achieve satisfactory flame retardance on either fabric. The previous study of phosphoric acid treated 50/50 and 65/35

TABLE XCIX

ISOPERIBOL DATA OF PVBr/THPC AND VBr/THPC TREATED BLENDS

<u>Source</u>	<u>Fabric</u>	<u>%R</u>	<u>ΔH_1, cal/gm</u>	<u>Rate cal/gm sec.</u>
SRRL	65/35 P/C, PVBr/THPC	21.8	1589	32.4 \pm 2.8
SRRL	50/50 P/Ry, PVBr/THPC	29.6	1162	26.6 \pm 2.0
Ethyl #18	50/50 P/C, 1% P	17.7	2034	54.2 \pm 1.5
Ethyl #2	50/50 P/C, 4.3% PVBr	18.3	1838	48.9 \pm 3.3
Ethyl #3	50/50 P/C, 7.0% PVBr	17.8	1820	46.8 \pm 3.4
Ethyl #6	50/50 P/C, 11.3% PVBr	18.3	1681	38.2 \pm 3.6
Ethyl #7	50/50 P/C, 21.2% PVBr	18.7	1442	32.6 \pm 3.4
Ethyl #9	50/50 P/C, 4.3% VBr/VC1	18.6	1939	50.2 \pm 4.3
Ethyl #11	50/50 P/C, 5.8% VBr/VC1	17.6	1904	45.8
Ethyl #14	50/50 P/C, 10.8% VBr/VC1	18.1	1841	46.6 \pm 2.0
Ethyl #16	50/50 P/C, 17.4% VBr/VC1	18.2	1634	45.5 \pm 2.4
Spring Mills	50/50 P/C	4.2	3006	57.5 \pm 3.3

900F cotton blends containing 3% bromine indicated that these blends should be self-extinguishing at about 2% phosphorus. Comparison of the THPC/PVBr treated polyester/cotton and the phosphoric acid treated 900F/cotton indicates that the bromine from the PVBr is probably somewhat less efficient than that from the 900F polyester. This is probably due to the low decomposition point of PVBr; however, it must also be noted that the use of PVBr introduces additional fuel into the system.

The results shown in Table XCIX and Figure 108 indicate that the retardant effect of PVBr is real and significant. The heat release of the THPC/PVBr treated 50/50 blends decreases consistently with increasing PVBr add-on. The rate of heat release also decreases as the amount of bromine increases. Similar results were obtained with the THPC/P(VBr/VC1) system, but the changes in rate and in total heat evolved were less, suggesting that the copolymer is less efficient than pure PVBr. The decreased efficiency may be due to the fact that the copolymer contains less bromine than the pure PVBr and that the chlorine is somewhat less effective. Another factor which may very well affect the flame retardant efficiency of the copolymer at its lower decomposition point than the PVBr.

In order to obtain a better evaluation of the importance of these effects, the PVBr and P(VBr/VC1) systems were compared by static oxygen bomb and isoperibol calorimetry. In the case of a strictly solid-phase system, previous data on treated 100% cotton had shown that both ΔH_1 and ΔH_2 decrease as a logarithmic function of %P content, and Table XCIX shows that the ratio $\Delta H_1/\Delta H_2$, is independent of the phosphorus content. Current data on PVBr and VBr/VC1 treated polyester/cotton blends indicate that the ratio $\Delta H_1/\Delta H_2$ for both systems decreases linearly with increasing halogen content as shown in Figure 109. Figure 110 shows that $\Delta H_2/(\Delta H_C^0)_F$ decreases as a function of increasing halogen content. Of perhaps greater significance, $\Delta H_2/(\Delta H_C^0)_F$ for both the PVBr and VBr/VC1 treated systems fall on the same line, indicating that the fuel-generating process (pyrolysis) is the same and not affected by the retardant. However, $\Delta H_1/(\Delta H_C^0)_F$ shows the difference in efficiency between the two systems, i.e. the PVBr treated system is slightly more efficient.

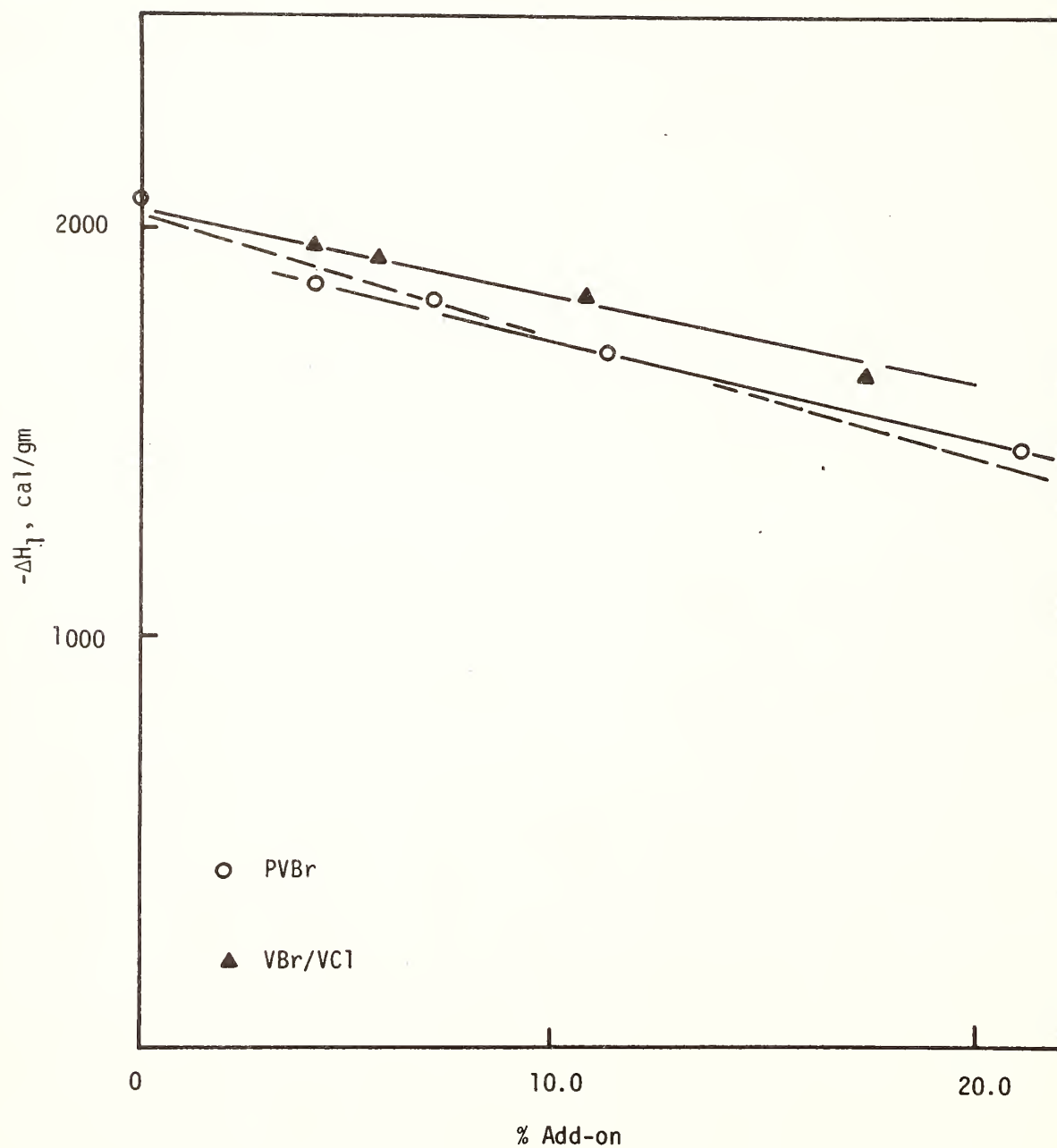


FIGURE 108. Variation of ΔH_f with %P of PVB and P(VBr/VCl) treated PET/cotton blends.

TABLE C
HEAT BALANCE IN FLAME RETARDANT TREATED COTTON SYSTEMS

%P	$-\Delta H_1^*$, cal/gm	$-\Delta H_2^*$, cal/gm	$\%(\frac{\Delta H_1}{\Delta H_2})$	$-\Delta H_3$, cal/gm	$\%(\frac{\Delta H_3}{\Delta H_2})$
0	3324	3688	90.1	436	11.8
<u>H₃PO₄</u>					
.56	2041	2218	92.0	301	13.6
.77	1823	1980	92.1	273	13.8
1.03	1623	1762	92.1	219	12.4
1.38	1422	1543	<u>92.2</u>	177	<u>11.5</u>
		Ave.	92.1		Ave. 12.8
<u>(NH₄)₂HPO₄</u>					
.49	2042	2342	87.9	337	14.5
.81	1649	1867	88.3	277	14.8
.93	1541	1741	88.5	265	15.2
1.11	1403	1580	<u>88.8</u>	246	<u>15.6</u>
		Ave.	88.4		Ave. 15.0
<u>THPOH-NH₃</u>					
.15	2852	3197	89.2	394	12.3
.53	2132	2392	89.1	297	12.4
.98	1781	2000	89.0	244	12.2
2.23	1311	1475	<u>88.9</u>	174	<u>11.8</u>
		Ave.	89.0		Ave. 12.3

* Smoothed values except for untreated cotton (0%P)

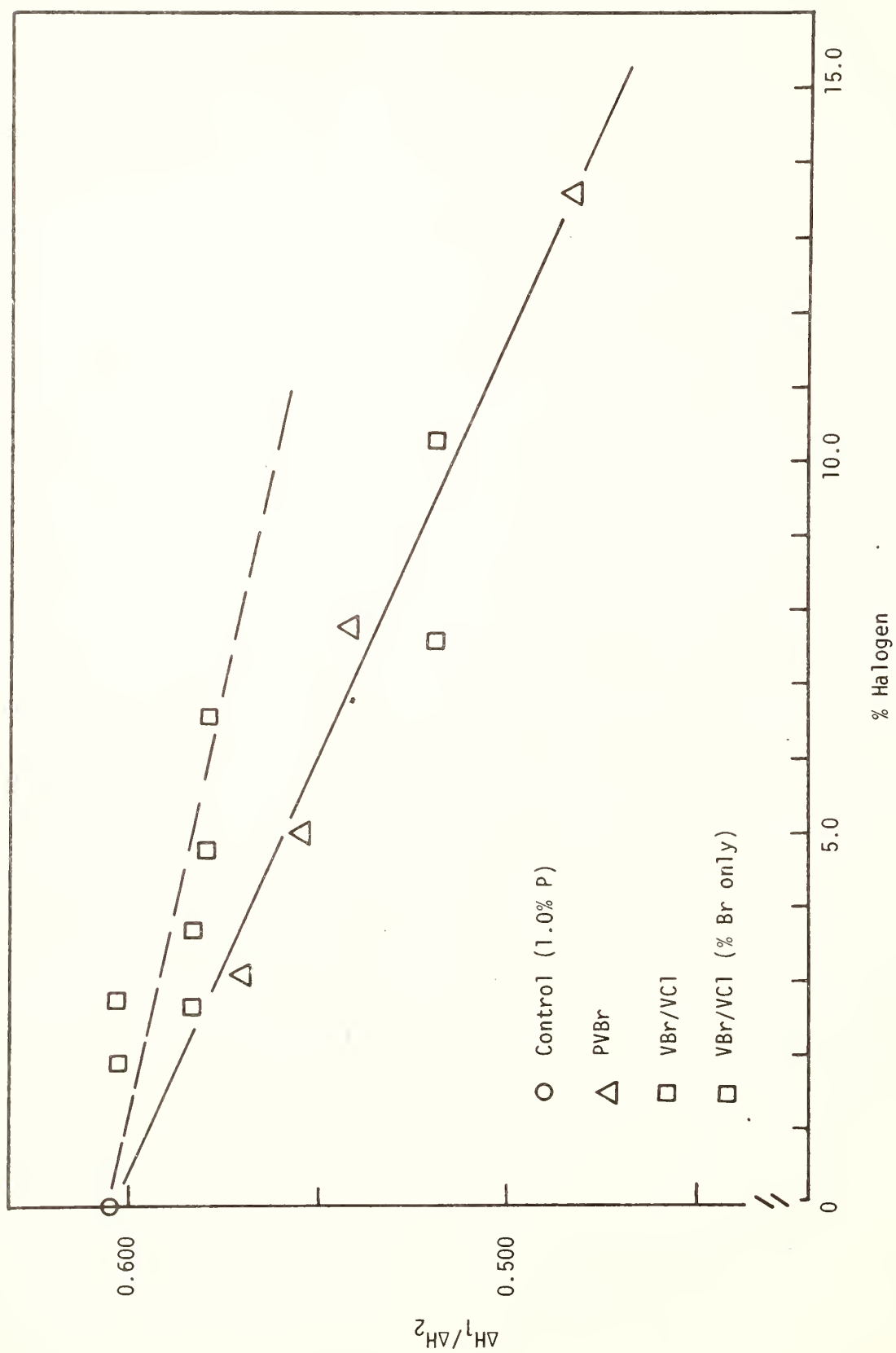


FIGURE 109. Dependence of $\Delta H_1/\Delta H_2$ on Br content of PVBr and P(VBr/VC1) treated 50/50 blends.

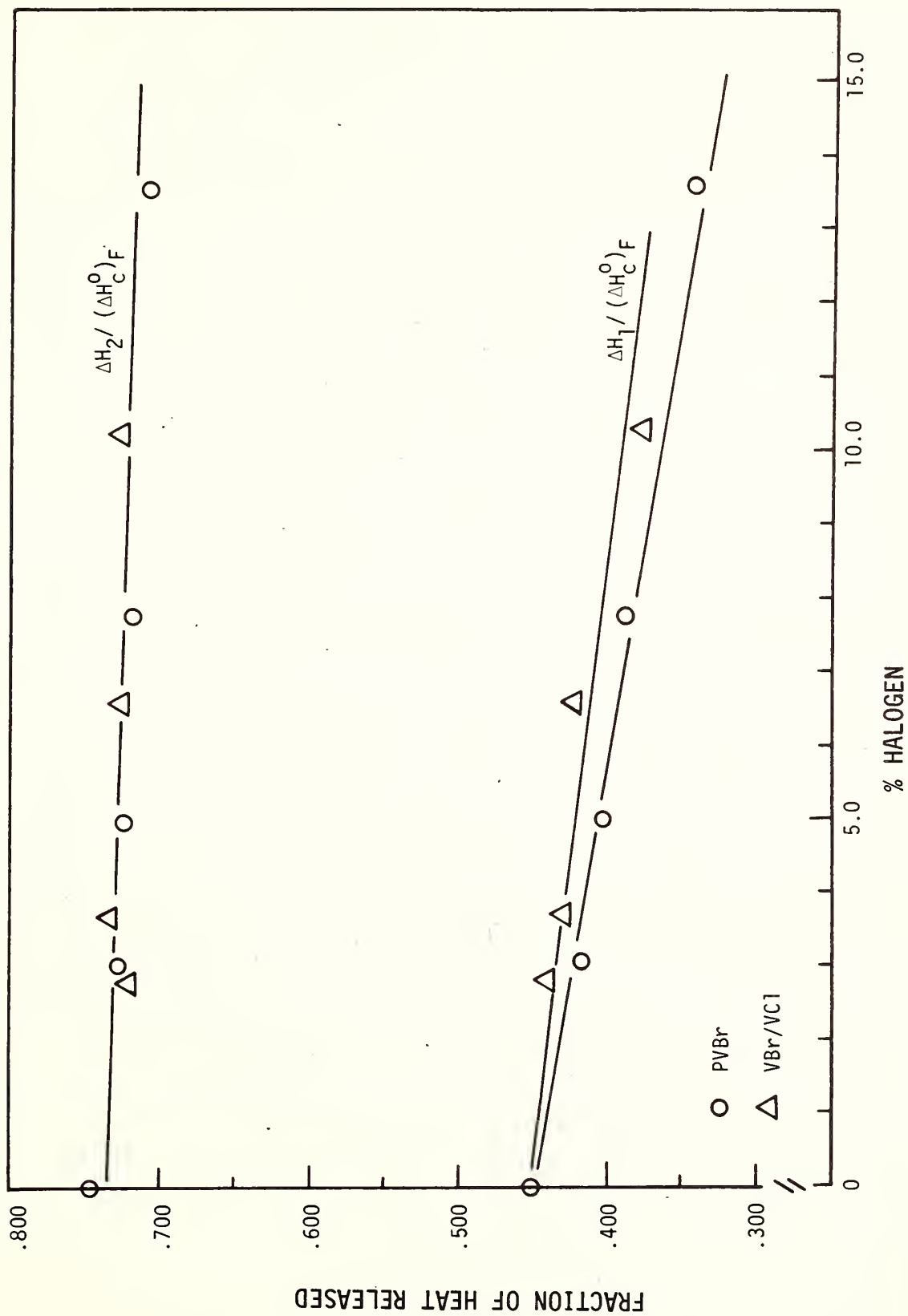


FIGURE 110. $\Delta H_1 / (\Delta H_C^\circ)_F$ and $\Delta H_2 / (\Delta H_C^\circ)_F$ from PBVr and P(VBr/VC1) treated PET/cotton blends.

Of considerable additional significance is the observation that char yields were not affected by the addition of either PVBr or the PVBr or the VBr/VCl copolymer. The char yields from the treated fabrics were identical to those of the controls; furthermore, oxygen bomb calorimetry on these chars revealed that the compositions of the chars were quite similar to that of the control, as would be expected for a vapor phase active retardant.

Comparisons of the data obtained on the VBr systems with those from the 900F/cotton blends show two significant differences (Figure 107). First the heat release values for both 900F/cotton and the PVBr/THPC treated polyester/cottons show linear dependency on the bromine content. However, the slope obtained with the 900F system is considerably steeper, indicating that the bromine from the 900F is, in fact, more effective. Secondly, the PVBr/THPC treated blends show no increase in char yield up to about 20% add-on while the 900F cotton system shows significant increase in char yield beyond that expected from phosphorus alone. These data indicate that bromine in the form of PVBr or its copolymers is probably active only in the vapor phase, whereas the aromatic bromine in the tetrabromobisphenol-A monomer of 900F could be active in both the PET and the cellulose. Alternatively, the increased residue could simply be the result of incomplete pyrolysis of the polyester due to the reduced heat liberated from the flame in the presence of a more efficient vapor phase active retardant. In any case, the difference in efficiency between the bromine in Dacron[®] 900F and PVBr is real and significant. This would suggest that improved formulations of the THPC/urea/PVBr type should be possible if bromine latexes could be found which have higher flame retardant efficiencies.

3.b. Determination of Flame Retardant Efficiencies of Bromine Compounds:

In order to provide the necessary data on flame retardant efficiencies of bromine compounds, a systematic evaluation by isoperibol calorimetry was undertaken. Since subjective evaluations had shown that decabromobisphenylene oxide in the presence of Sb_2O_3 (FR P-44[®]) was

a particularly effective system, it was the next one chosen for more detailed study. The heat release from fabrics treated with this formulation is shown in Figure 34. Values of heat release from these fabrics with and without grid support, decrease linearly with increasing Br content. Linear regressions of $-\Delta H_1$ vs % Br are tabulated in Table CI. The linear regression gave a slope of 228.2 cal/gm-%Br on the 50/50 blend. This is essentially identical to the regression slope obtained on the 100% cotton fabrics without support. This suggests that P-44 has identical efficiency on all three different fabrics when burned without support. In other words, the efficiency of P-44[®] is not substrate-dependent which can be taken as an indication of vapor-phase retardant action. With a grid support, $-\Delta H_1$ of 100% cotton gave a regression slope of 193.6 cal/gm-%Br which is slightly lower, but not significantly different from the slope of the data obtained without support. However, data from the 50/50 blend gave significantly larger slopes when burned with support, 292.4 cal/gm-Br vs 228.2 cal/gm-Br.

Of course, the conclusions relating to optimum formulations which can be drawn from these experiments are highly dependent on the efficiency of the bromine-containing retardant. Thus it becomes necessary to characterize the flame retardant efficiencies of a variety of bromine-containing structures. Several series of fabrics treated with bromine retardants were therefore examined by isoperibol calorimetry.

A plot of net heat reduction, $\Delta H_1 - (\Delta H_1)_{\text{control}}$, vs Br content is shown in Figure 35. This plot is essentially the same as that in Figure 34, but with the differences in ΔH_1 of various control fabrics normalized. Linear regression of various groupings of these data were taken and the regression results are tabulated in Table CII. These results indicate that the best regression fit on the basis of intercept and the standard deviation of the slope is obtained when all fabrics with or without grid are fitted on the same line. This tends to suggest that the grid support has no effect on the efficiency of P-44[®]. The scattering of data among the results is obvious, and is

TABLE CI
 LINEAR REGRESSION OF HEAT RELEASE FROM P-44[®] TREATED FABRICS

Heat Release: $-\Delta H_1 = A + B(\%Br)$

Fabric	A*	B, cal/gm-%Br	r
W/O Grid			
100% Cotton	-3329(3334)	226.2 ±20.4	.9802
50/50	-3004(2942)	258.2 ±36.0	.9624
65/35	-2743(2846)	193.4 ±19.0	.9813
50/50 and 65/35	-2872(2942,2846)	228.2 ±21.5	.9602
W/ Grid			
100% Cotton	-3485(3424)	193.6 ±29.3	.9571
50/50	-3485(3460)	292.4 ±14.7	.9962

* Values in parentheses are $-\Delta H_1$ of the controls.

TABLE CII

 LINEAR REGRESSION OF NET HEAT REDUCTION FROM P-44[®] TREATED FABRICS

$$\text{Net Heat Reduction: } \Delta H_1 - (\Delta H_1)_{\text{control}} = A + B(\%Br)$$

Fabrics	A	B, cal/gm-%Br	r
W/O Grid	11	228.7±14.7	.9666
All Fabrics			
W/ Grid			
100% Cotton	-61	193.6±29.3	.9571
50/50	-25	292.4±14.7	.9692
50/50 W/ and W/O Grid	-40	272.1±23.0	.9692
All Fabrics W/O Grid			
and 100% Cotton W/grid	-13	222.6±15.2	.9503
All Fabrics W/ and W/O Grid	-17	234.6±15.6	.9430

probably due to uneven treatment of P-44[®] on the fabrics.

Two additional series of fabrics, 100% cotton and 50/50 blend, treated with the decabromobiphenylene oxide without the Sb₂O₃ (FR P-53[®] from White Chemical Company) were obtained and studied. Calorimetric results from the fabrics treated with P-53[®] are tabulated in Table CIII. Heat release data are shown in Figure 111 plotted vs Br content. Data from previously obtained P-44[®] treated fabrics are also included for comparison. Values of heat release of both the P-53[®] treated 100% cotton and 50/50 blend are linearly dependent on % Br, with the variation in the data slightly larger for the 50/50 blend. Linear regression of both sets of data are shown in Table CIV. Data from the P-53[®] treated blend exhibit a slightly smaller slope than from 100% cotton. However, both P-53[®] treated fabrics exhibited much smaller slopes than those treated with P-44[®]. Linear regressions were also obtained for net heat reduction. The best fit for P-53[®] treated fabrics, based on the intercept, A, and the standard deviation of the slope, B, occurs when both sets of data are fitted on the same straight line with a slope of 108.6 cal/%Br. This is less than a half of the slope for the P-44[®] treatment. The effect of antimony in P-44[®] is very profound. Plots of net heat reduction vs % Br for both the P-44[®] and P-53[®] treated fabrics are shown in Figure 112.

Efficiencies of all bromine-containing retardants studied are compiled in Table CV. P-44[®] clearly is the most efficient system but, unfortunately, it is not amenable to use with THPC or other phosphorus treatments. Phosphorus is known to exhibit an antagonism toward antimony/halogen systems. As expected, this antagonism was encountered when the P-44[®] was used to top fabrics treated with a THPS[®]/urea finish.

3.c. Utilization of Other Bromine Compounds with Phosphonium Salts:

In an effort to develop more efficient bromine sources for use in lieu of PVBr or the VBr/VC1 copolymers, a series of structures

TABLE CIII

P-53 [Ⓡ] TREATED BLEND FABRICS (W/O GRID SUPPORT)

<u>% FINISH</u>	<u>% Br</u>	<u>% Br (owf)</u>	<u>$-\Delta H_1$, cal/gm</u>	<u>$\Delta H_1 - \Delta H_{1,control}$</u>
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100% COTTON

Control	--	--	3334	--
8.19	3.94	4.29	2864	470
14.94	7.42	8.72	2436	898
24.84	9.49	12.63	2168	1166
32.51	13.28	19.68	1832	1502
44.67	15.18	27.44	1562	1772

50/50 PET/COTTON

Control	--	--	2942	--
9.18	4.50	4.95	2348	594
15.91	7.34	8.73	2384	558
25.09	9.61	12.83	1936	1006
45.96	14.23	26.33	1549	1393

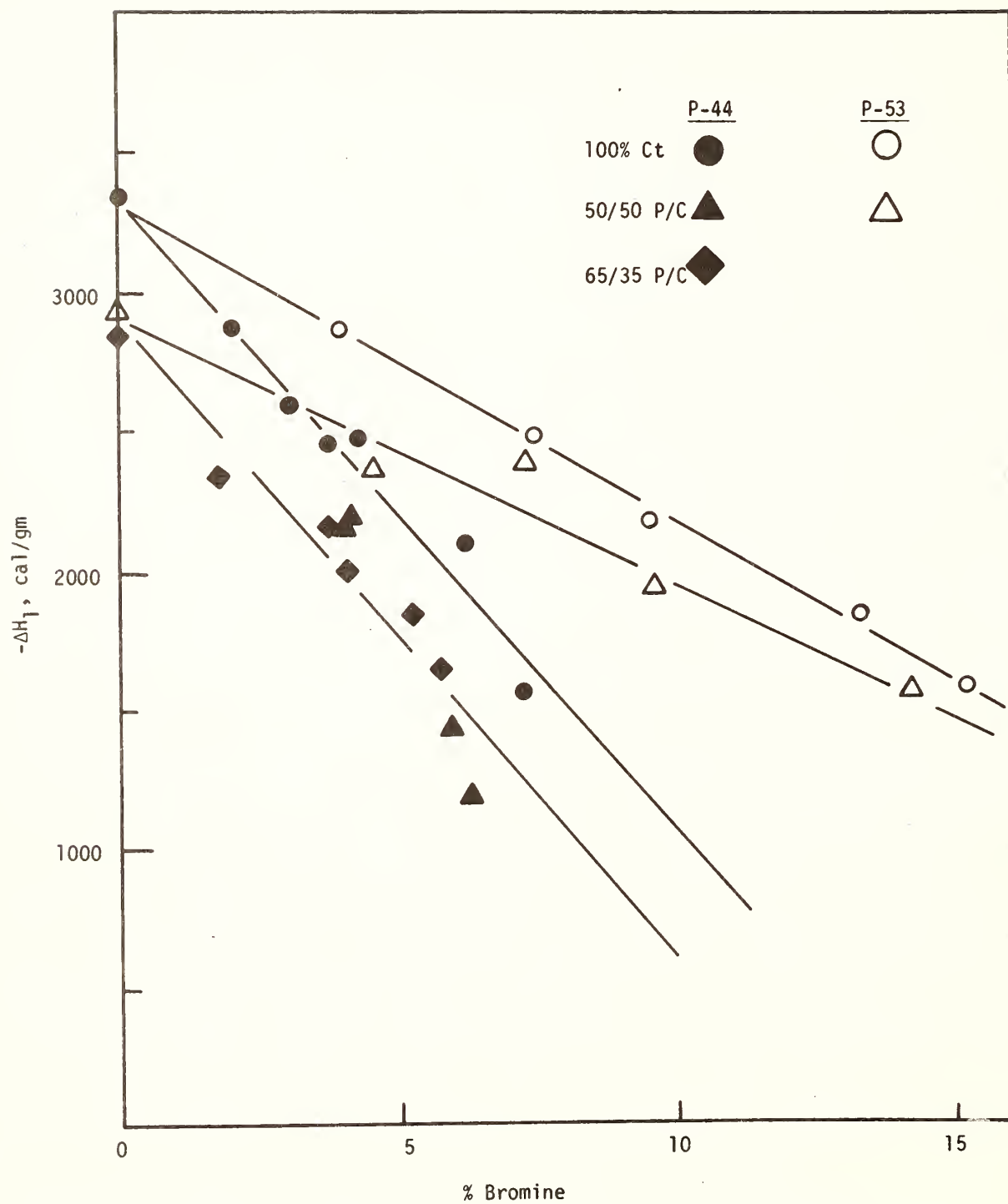


FIGURE 111. Heat release of P-44^(R) and P-53^(R) treated fabrics.

TABLE CIV
EFFICIENCIES OF P-44^(R) AND P-53^(R) TREATED FABRICS

$$-\Delta H_1 = A + B(\%Br)$$

Fabric	A	B, cal/gm-%Br	r
P-44 ^(R) Treated			
100% Cotton	-3329	226.2 ± 20.4	.9802
50/50 and 65/35	-2872	228.2 ± 21.5	.9602
P-53 ^(R) Treated			
100% Cotton	-3313	115.3 ± 3.0	.9986
50/50	-2913	95.5 ± 12.3	.9758

$$\Delta H_1 - (\Delta H_1)_{\text{control}} = A + B(\%Br)$$

Fabric	A	b, cal/gm-%Br	r
P-44 ^(R) Treated			
All Fabrics	11	228.7 ± 14.7	.9666
P-53 ^(R) Treated			
100% Cotton	21	115.3 ± 3.0	.9986
50/50	29	95.5 ± 12.3	.9758
All Fabrics	12	108.6 ± 7.4	.9796

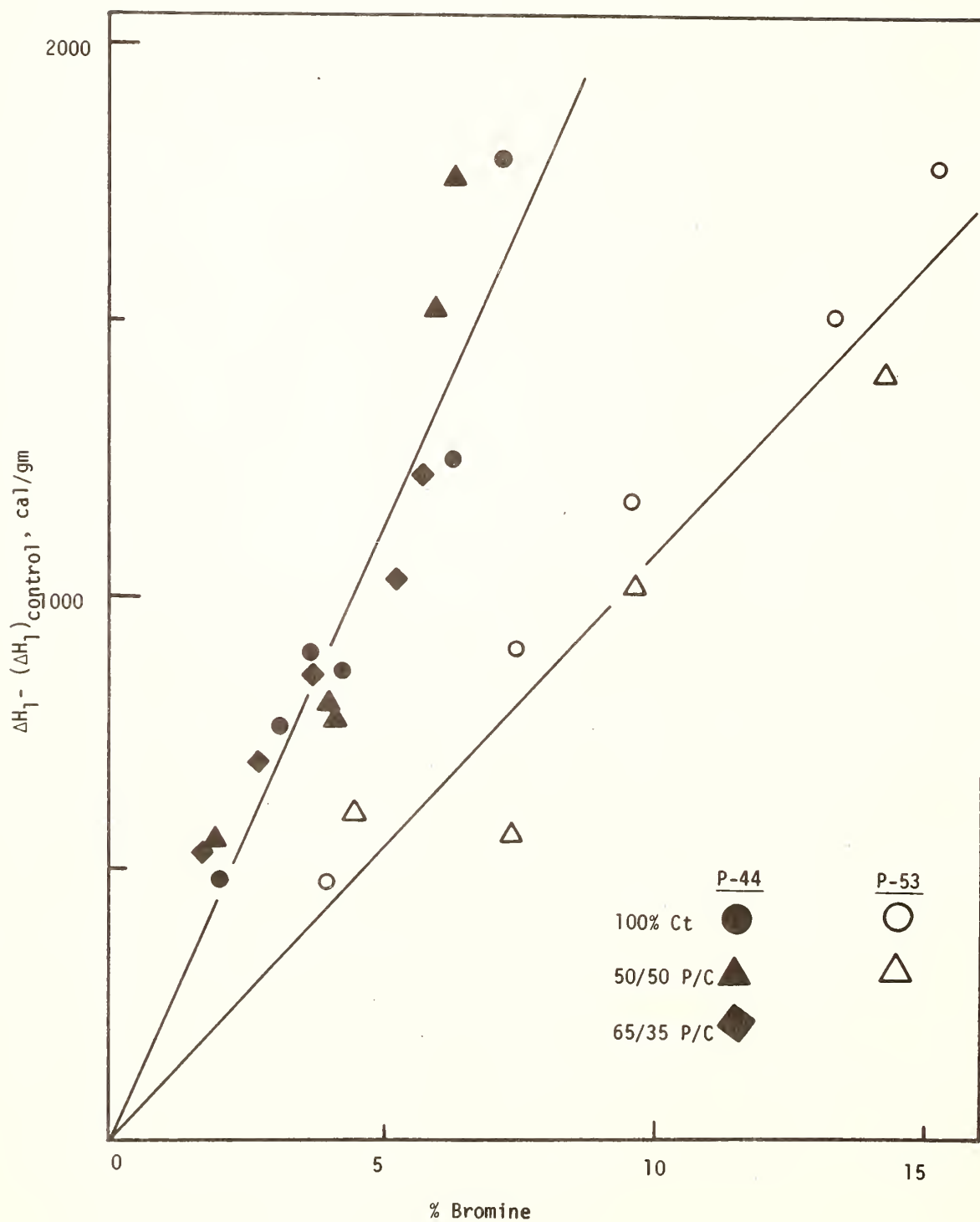


FIGURE 112. Net heat reduction from P-44^(R) and P-53^(R) treated fabric

TABLE CV

EFFICIENCIES OF BROMINE - CONTAINING RETARDANTS

$$\Delta H_1 - (\Delta H_1)_{\text{control}} = A + B(\%Br)$$

Retardant	Fabrics	A	B, cal/gm-%Br	r
^(R) P-44	100% Cotton, 65/35, 50/50 P/C Blends	11	228.7 ± 14.7	.9666
^(R) 900F	75/25, 65/35, 50/50, 900F ^(R) /Ct Blends	-8	126.5 ± 14.0	.9880
^(R) P-53	100% Cotton, 50/50 P/C Blend	12	108.6 ± 7.4	.9796
^(R) T23P	50/50 P/C Blend	-7	93.5 ± 0.9	.9999
PVBr	50/50 P/C Blend	-11	61.2 ± 3.4	.9953
P(VBr/VC1)	50/50 P/C Blend	0	60.3 ± 5.5	.9877

$$\Delta H_1 - (\Delta H_1)_{\text{control}} = \text{Net Heat Reduction}$$

A B = Regression Constants

r = Correlation Coefficient

related to dibromocyanoacetamide was prepared and evaluated. Dibromocyanoacetylurea has been synthesized and applied to 50/50 blend fabric in conjunction with THPC. An 18% add-on was achieved to yield a sample exhibiting an OI value of 29.0 and a BOI 23.0. This material showed a significant weight loss in an oven at 110°C for thirty minutes due to possible steam distillation of the material. Attempts to fix the material by cross-linking with urea, Aerotex 23[®], and dimethylol dihydroxyethylene urea resins resulted in gross discoloration. There was also a marked loss in flame retardant characteristics following either drying or cross-linking. The treated fabric was noticeably hygroscopic in the absence of resin treatments.

More promising results were obtained with dibromoacetamide which was prepared by hydrolyzing dibromoacetonitrile. A white crystalline product with a melting point of 152°-154°C was obtained. This material melted with no evidence of decomposition. A weight loss was observed in the region 130°-145°C by TGA, presumably due to sublimation of the compound. The dibromoacetamide was padded on to 50/50 blend fabric to produce a sample which showed no discoloration upon heat treatment for three minutes at 150°C. However, this fabric exhibited very low flame retardant efficiency as either the free amide or its N-methylol derivative. Complexation of the amide with 2 moles of THPC produced a reagent with improved retardant characteristics but attempts to fix the retardant into a durable finish failed.

Other attempts to produce reactive bromo compounds included the bromination of cyanoacetylpiperidine which failed to yield an isolable product and the synthesis of bromocyanoacetyl urethane which led to a product with a melting point of 78-80°C. This latter material showed considerable decomposition at 150°C on a 50/50 blend fabric. The compound itself decomposed slowly with evolution of HBr.

Better results were obtained using dibromomalondiamide. This material was found by TGA to be stable to 175° and exhibited good flame retardance on blend fabric. N-methylation of the material was achieved readily and the resulting product appeared stable to heat. However no fix could be obtained with this material.

Since it would seem that the hydrolytic stability of the dibromomalondiamide might be the subject of concern, an investigation was carried out to determine its stability toward base. After three hours in a water slurry no evidence of HBr evolution could be found. The pH of the slurry was then raised to approximately 10 using sodium hydroxide and the slurry allowed to stir overnight. During this time the pH dropped to approximately 8 indicating some loss in HBr from the material. A large quantity of the water-insoluble diamide remained however, indicating the retention of most of the bromine. On this basis an attempt was made to develop a formulation suitable for larger scale fabric evaluations based on the THPC adduct of the diamide but only limited success was achieved.

The dibromomalondiamide (DBMA) was also evaluated as a co-reactant for phosphorus containing flame retardants. The compound was padded on to 50/50 fabric along with Fyrol 76[®] to produce an excellent flame retardant fabric but no cure could be obtained with persulfate catalyst. Better results were obtained using the bromo compound in the form of its complex with 2 moles of THPC. This produced good flame resistance and after curing the finish exhibited limited durability to a normal process wash. Attempts to improve the durability by fixation with a variety of nitrogenous resins led to extensive discoloration on curing. The solubility problems encountered with DBMA were overcome by N-methylation to produce a water soluble species. This was applied to 50/50 blend fabric using a non-nitrogenous resin based on formaldehyde (Tetraset ST-1[®] from Riegel Textile) and cured for 30 seconds at 165°C. These samples discolored strongly. Experiments were also run using the N-methylol DBMA (1) by itself, (2) with Tetraset ST-1[®], (3) with THPC and (4) with THPC and Tetraset ST-1[®]. These were cured at 150° for 1, 2, and 3 minutes. All of the fabrics discolored to varying degrees with those containing THPC giving the most pronounced color formation.

The brominated amides were therefore abandoned and attention turned to efforts to develop a bromine-containing latex more suitable than PVBr or P(VBr/VC1) for application in conjunction with phosphonium salt

finishes. As previously reported, techniques were devised for the emulsion polymerization of DBPA and TBPOEA. The DBPA latex contained approximately 40% solids as it was prepared and was suitable for direct application to fabrics. The same recipe was inappropriate for either VBr_2 or TBPOEA. In both of these latter cases, polymerization was effected but no stable emulsion could be prepared.

In one series of experiments, fabrics previously treated with Pyrovatex CP[®] and THPC/urea finishes were over-treated with poly(vinylidene bromide) or with the P(DBPA) latex. Based on OI and vertical flame test results, these finishes were not as effective as those based on Fyrol 76[®] and the bromine compounds. The latex was also applied to the 50/50 ETIP fabric using the formulation in Table CVI. The resulting fabrics exhibited borderline flame retardancy and limited durability. When a slightly heavier fabric was used with the same formulation an initial char length of 5.1 in. was observed. This fabric exhibited a borderline failure after 50 launderings. The samples had a harsh, stiff hand and suffered from noticeable strength loss. At this point the materials were turned over to the Research Committee of the Palmetto Section, AATCC. This group, composed of representatives from United Merchants and Manufacturers, M. Lowenstein and Sons, the Graniteville Co., C. S. Tanner Co., Emery Industries, C. H. Patrick and Co., and Clemson University, has undertaken a comprehensive study of the P(DBPA) latex and is currently working to evaluate the feasibility of using this latex in conjunction with a THPS[®]-urea finish. A series of samples were treated with THPC-urea P(VBr/VCl) by Dr. John Holston of M. Lowenstein and Sons using the procedure of Donaldson and co-workers (57) and compared to a similar series prepared in the same way except for the replacement of the P(VBr/VCl) by P(DBPA). The results are shown in Table CVII. Satisfactory flame resistance was not obtained with either finish when evaluated by the criteria of FF 3-71; however all of the samples were found to fall into Class I using the MAFT. On this basis, it would seem probable that satisfactory performance in FF 3-71 could be obtained with either formulation using a heavier weight fabric or a fabric containing softer

TABLE CVI
FORMULATION FOR THPS[®]/P(DBPA) FINISH

Solution A:	THPS [®]	300 g
	Resloom [®] HP	100 g
	H ₂ O (180°)	100 g
Solution B:	DBPA latex (43% solids)	350 g
	Trycol [®] OP-407 (50% soln)	3 g

Dilute solution B to 500 cc, add solution A, dilute to total volume of 1 liter.

TABLE CVII

Sample	Wet pick-up	Initial average	Individual char length (in)	Average after flame	Tensile strength (lbs, W&F)	Tearing strength (lbs, W&F)
THPC ^(R) Urea - P(VBr/VC1)	90%	8.4	(8.6,10.0,3.2x10.0,10.0)	23	91 x 49	3.3 x 1.6
"	101%	4.6	(3.0,3.2,3.6 x7.4,5.9)	6	90 x 49	3.6 x 1.6
"	111%	8.2	(10.0,10.0,6.6x10.0,4.3)	22	87 x 53	2.8 x 1.5
THPC ^(R) Urea - P(DBPA)	90%	5.9	(3.1,4.9,6.1 x5.4,10.0)	23	89 x 49	3.1 x 1.8
"	100%	5.7	(4.4,3.5,4.1 x10.0,6.5)	35	91 x 55	2.9 x 1.5
"	111%	4.7	(3.6,2.8,3.5 x3.6,10.0)	6	83 x 52	2.8 x 1.5
THPC ^(R) - Urea - P(DBPA) with melamine	90%	8.0	(5.5,10.0,10.0x4.7,10.0)	28	86 x 51	2.6 x 1.4
"	98%	3.9	(3.5,3.3,4.8 x4.0,4.0)	15	85 x 50	2.6 x 1.4
"	112%	3.0	(2.7,3.3,3.2 x2.9,3.1)	5	83 x 54	2.2 x 1.4

yarns.

In a concurrent series of experiments conducted by Mr. Charles Bailey of the Graniteville Company, a number of modified formulations for this finish were evaluated. Donaldson and co-workers (57) had previously recommended the incorporation of resins such as trimethylol-melamine or trimethylolglycourea to improve the fixation efficiencies of soft latex systems. Thus a series of samples was prepared using the same formulation except for the addition of 4.0 weight % (owb) of Aero-tex[®] Resin M-3 in with the THPC-urea- Na_2HPO_4 bath component mix prior to addition to the P(DBPA) latex. The results from these experiments are also given in Table CVII. These data would seem to indicate that the achievement of higher fixed add-ons should lead to a satisfactory performance level. Thus attention was focused on efforts to modify the P(DBPA) formulations to increase the efficiency of fixation. Both pad-dry-heat cure and pad-dry-ammonia cure processes were evaluated. Three different phosphonium systems were studied in combination with five different resins and two different catalyst systems.

Many of the formulations failed to give sufficient fixation to produce satisfactory flame resistance, but several were found which showed considerable promise. Representative results are shown in Tables CVIII and CIX. The melamine resin by itself appeared to give sufficiently effective fixation to allow the more easily finishable fabrics to pass FF 3-71; however, with the more finish-resistant poplin it was necessary to include both the melamine and urea to produce a durable treatment capable of passing the vertical test after 50 home launderings.

Unfortunately, these finishes with the high resin contents yield fabrics which are significantly stiffened. Attempts to alleviate this problem with a variety of standard softeners have not proved successful to date. Better results appear to be obtained using reactive silicone softeners. Incorporation of Dow-Corning 1111 Emulsion[®] into the formulation produced a significant improvement in the fabric hand but detracted somewhat from the flame resistance.

It would also appear tht the hand of these fabrics could be im-

TABLE CVIII

Pad Bath Formulation I for Phosphonium Condensate and P(DBPA)

Phosphonium Condensate (1)	300 gm/l
TMM (2)	100 gm/l
Urea	100 gm/l
Amine Hydrochloride (3)	20 gm/l
P(DBPA) (4)	350 gm/l
Wetting Agent (5)	10 gm/l

	50/50 poplin	50/50 denim	65/35 twill
Wet Pick-up	113%	69%	71%
Tensile (warp)	100	175	1.9
Tear (warp)	3	4.6	5.5
Wrinkle Recovery (w&f)	223	---	---
<u>Char Length (in)</u>			
initial warp	3.3	0.8	1.3
fill	5.6	0.7	0.4
50 HL, warp	2.6	0.8	0.9
fill	3.1	0.8	1.1
<u>After Flame, sec</u>			
initial warp	18	0	0
fill	19	0	0
50 HL, warp	16	0	0
fill	18	0	0

(1) Fireaway 2[®]

(4) Dur-o-cryl BL-1

(2) Valmel 40[®](5) Valdet 4016[®](3) Valcat AH0[®]

Phosphonium Condensate (1)

TMM (2)	100 gm/l
Amine Hydrochloride (3)	20 gm/l
Wetting Agent (4)	10 gm/l
P(DBPA) (5)	350 gm/l

	50/50 poplin	50/50 twill	65/35 twill
% Wet Pick-up	114%	69%	70%
Tensile (warp)	99	214	219
Tear (warp)	3.7	9.5	7.9
Wrinkle Recovery (w&f)	267	---	---
<u>Char Length (in)</u>			
initial warp	3.5	1.0	1.2
fill	5.7	1.3	2.4
50 HL, warp	BEL	1.4	1.9
fill	BEL	1.0	1.3
<u>After Flame, sec</u>			
initial warp	25	1.0	1.0
fill	7	0	12
50 HL, warp	BEL	4	19
fill	BEL	4	0

- (1) Fireaway 2[®]
 (2) Valmel 40[®]
 (3) Valcat AH0[®]
 (4) Valdet 4016[®]
 (5) Dur-o-cryl BL-1[®]

proved by mechanical action. A scanning electron microscopy study showed significant fiber-fiber bonding resulting from the latex treatment. This type of bonding is frequently responsible for stiffening effects of surface finishes and can usually be markedly reduced by mechanical breaking.

This and other factors affecting the commercial utility of the THPS[®]-urea-P(DBPA) finish will be the subject of a study to be initiated in the near future at SRRC.

4. Systems Based on a Bromine-containing Phosphazene

A somewhat different approach to incorporating phosphorus and bromine in one system has been taken by Sandoz Colors and Chemicals who have developed a flame retardant based on a bromine-containing phosphazene. This material, when applied to polyester/cotton blends in conjunction with a resin such as hexamethoxymethylol melamine, has been found to produce an effective and durable treatment. In this form the treatment was found to impart a stiff hand to the fabric. Although this hand would be improved by mechanical action, a series of experiments was undertaken in cooperation with Sandoz in an attempt to find a non-mechanical solution to the hand problem.

Electron micrographs of fabrics treated with the Sandoz 1030 finish with and without resin indicated that the hand problem is related to the physical properties of the film it forms on the individual fibers during curing. There was no evidence in the micrographs of significant fiber-fiber bonding, even with the resin present. Consequently efforts were focused on modifying the physical properties of this film. The Dow-Corning silicone emulsions, which are also film formers, were found to offer some promise in solving these hand problems by plasticizing the flame-retardant films. It was found that a rather heavy loading of Dow-Corning 1111[®] emulsion gave a good soft hand to fabrics prepared in the laboratory and line dried or tumble dried.

However, unexpected difficulties were encountered with fabrics prepared in the laboratory but dried and cured under conditions similar to those which might be expected in the pilot plant. Fabrics dried under these conditions (150°C for 2 min. in the Dispatch oven) were essentially as stiff as those prepared without the silicone. This phenomenon is completely reversible and the stiff fabrics can be softened by wetting thoroughly followed by line drying or tumble drying. Similarly, the soft fabrics can be stiffened by subjection to heat in the form of oven drying or ironing (dry or steam using the durable press setting). Since it was thought that this problem might be the result of overdrying and loss of moisture which could act as a

plasticizer for the fiber coating. However, experiments in which treated fabric samples were dried down to different moisture contents at various temperatures indicated that this was not the case.

In an attempt to define the origin of the fabric stiffness differential scanning calorimetry was performed on a series of cast films containing the Sandoz 1030/190; the Sandoz 130/190 plus resin and accelerator, the Sandoz 1030/190 plus resin and accelerator and Dow Corning 1111[®] emulsion, and the Sandoz 1030/190 plus resin and accelerator and Dow Corning 1111[®] emulsion and Trycol[®] OP-407 (an ethylene oxide-actapheno derivative).

The films were cast from formulations, similar to those which might be used in an actual application. The films were dried overnight at 40°C in a forced air oven and then cured at 120°C for 4 hours.

The thermograms for all of the above films were very similar. This is demonstrated by Figure 113 where the DSC for the 1030/190 plus resin and accelerator is compared to that obtained from the film with the DC-1111[®] and the Trycol[®] OP-407. All of the films were characterized by a broad endotherm at $\approx 60-80^{\circ}\text{C}$ followed by the onset of the exothermic decomposition of the phosphazene at $\approx 180^{\circ}\text{C}$. The assignment of these thermal transitions as melting and decomposition respectively was supported by thermogravimetric analysis. This is shown by Figure 114 where no weight loss is observed in the region 60-80°C whereas the major weight loss begins at $\approx 180^{\circ}\text{C}$.

Despite the fact that the thermal responses of the films showed no significant differences, their physical properties were quite dissimilar. The film containing the 1030/190 plus resin and accelerator was very hard, clear and brittle. When the DC-1111[®] was added to the formulation the film became opaque, was not quite as hard and was much easier to chip and powder. With both the DC-1111[®] and Trycol[®] OP-407 present, the film became rubbery and opaque. Not surprisingly when the formulation containing the DC-1111[®] and Trycol[®] OP-407 was applied to a 7.5 oz/yd² brushed denim a significant improvement in hand was observed after the cure. However, the highly water soluble Trycol[®] OP-407 was lost in the afterwash resulting in a fabric with the same aesthetics as was obtained by using the DC-1111[®] formulation

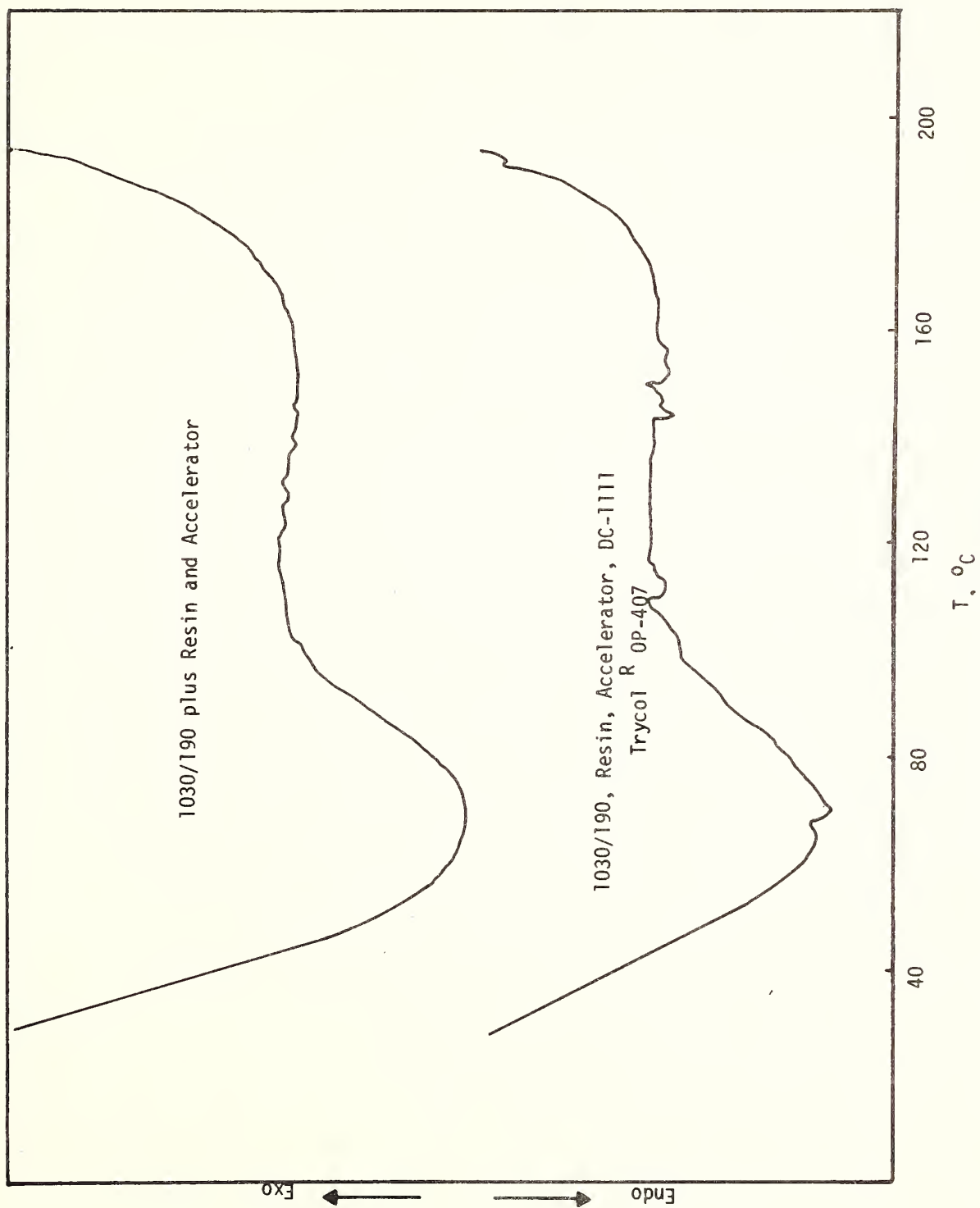


FIGURE 113. Comparison of Sandoz 1030/190 film DSC results.

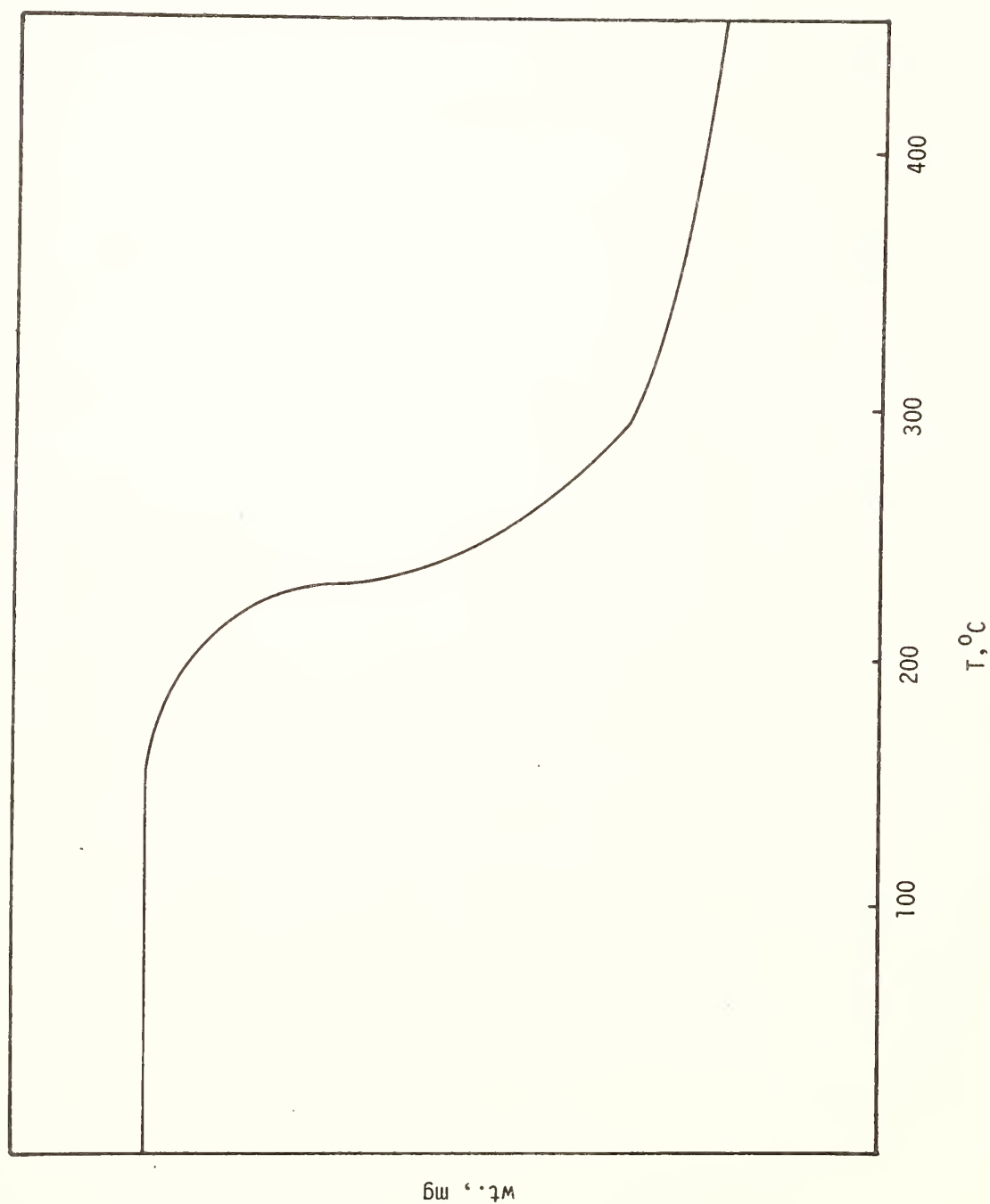


FIGURE 114. TGA of Sandoz 1030/190 plus resin and accelerator film.

alone.

On the basis of these observations it was concluded that the hand problem of the 1030/190 finish could probably be overcome if a durable material which was able to plasticize the flame retardant film like the Trycol[®] OP-407 could be found. Although several formulations containing several different classes of materials (including other Dow Corning reactive silicones) were tried, as shown by the data in Table CX a sufficient degree of plasticization was not achieved.

An alternative non-mechanical solution to the hand problem would be to change the inherent physical characteristics of the FR 1030/190 itself. If the melting point of the FR 1030/190 was increased to some temperature slightly above any temperature the treated fabric might encounter after the cure step, the tough continuous film would not reform after afterwashing. Sandoz is currently investigating the possibility of such a modification of FR 1030/190.

Calorimetric studies were also conducted with the Sandoz 1030 finish. Isoperibol calorimetric data are presented in Figure 115. As shown in Figure 115 the heat release as a function of % Br shows the deviation from linearity typical of condensed phase flame retardants. This, of course, results from the presence of the phosphorus. The combined P and Br effect of this system is shown more clearly in Figure 116 where the Sandoz 1030 results are plotted as a function of % P and compared to the earlier calorimetric data on the H₃PO₄ treated 900F[®] Cotton 50/50 blend fabrics. This is also reflected in the ETIP 50/50 blend treated with P-44[®]; by comparison, the Sandoz finish passes easily at only 6.3% Br.

TABLE CX

Effect of Some Selected Additives on the Film Properties of

Sandoz 1030/190 with Resin and Accelerator

Additive	Type	Film Properties	7.5 oz/yd ² brushed Denim	Durable ⁽¹⁾
None	----	clear, brittle	stiff, difficult to break	Yes
DC-1111 ^(R)	reactive silicone	opaque, very brittle	stiff, easily broken	Yes
Trycol ^(R) OP-407 ⁽¹⁾	ethoxylated octaphenol	clear, rubbery	soft	No
DC-8026 ^(R)	reactive silicone	clear, tough	stiff, difficult to break	Yes
Fabritone ^(R) 5000	monionic softener	clear, tough	stiff, difficult to break	Yes
Fabritone ^(R) C-7346	monionic emulsion	opaque, brittle	not applied	---
Trylox ^(R) HCO-25	hydrogenated castor oil	clear, tough	not applied	---

⁽¹⁾ 50 Home Launderings.

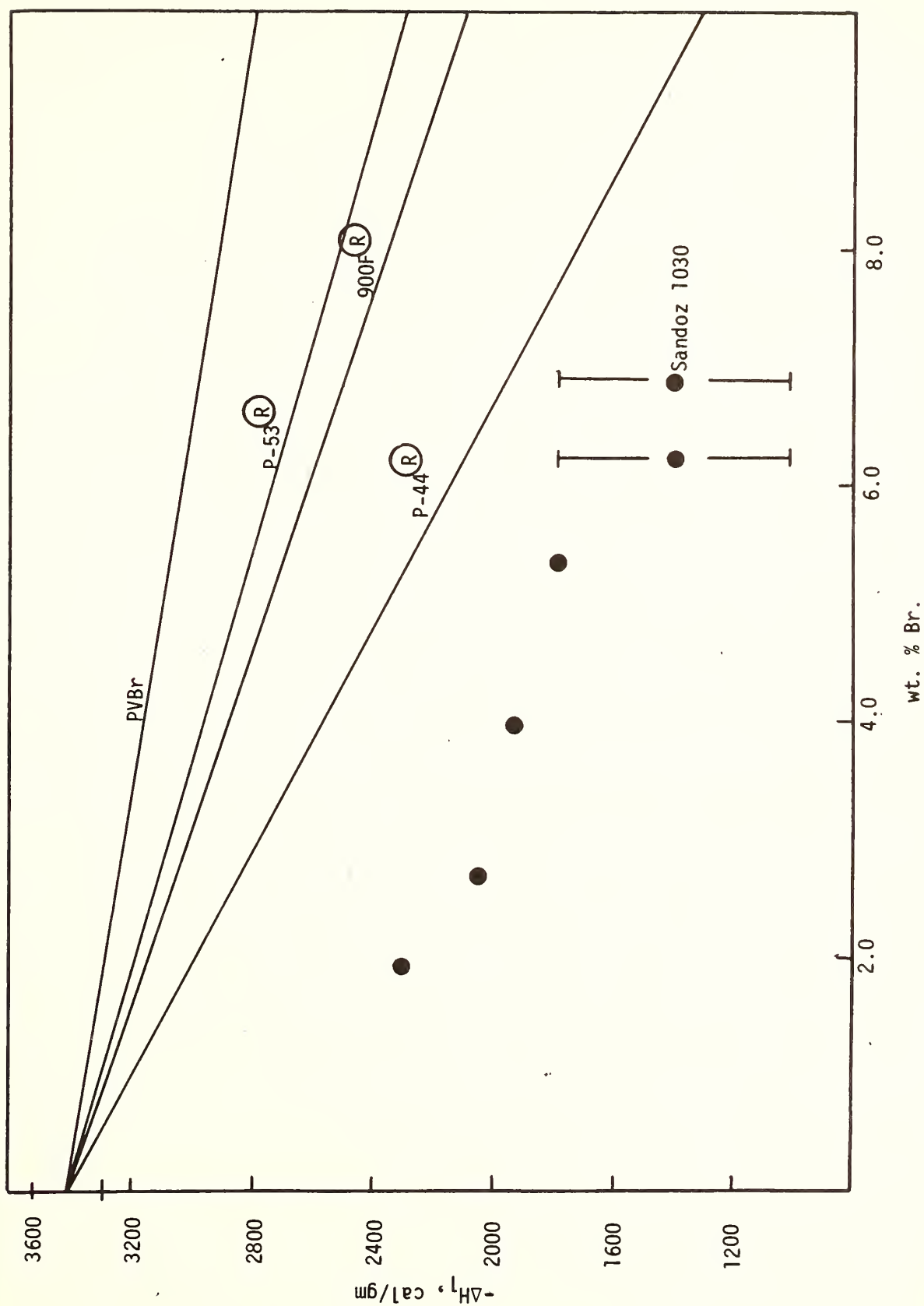


FIGURE 115. Heat release from Sandoz 1030 as a function of Br content.

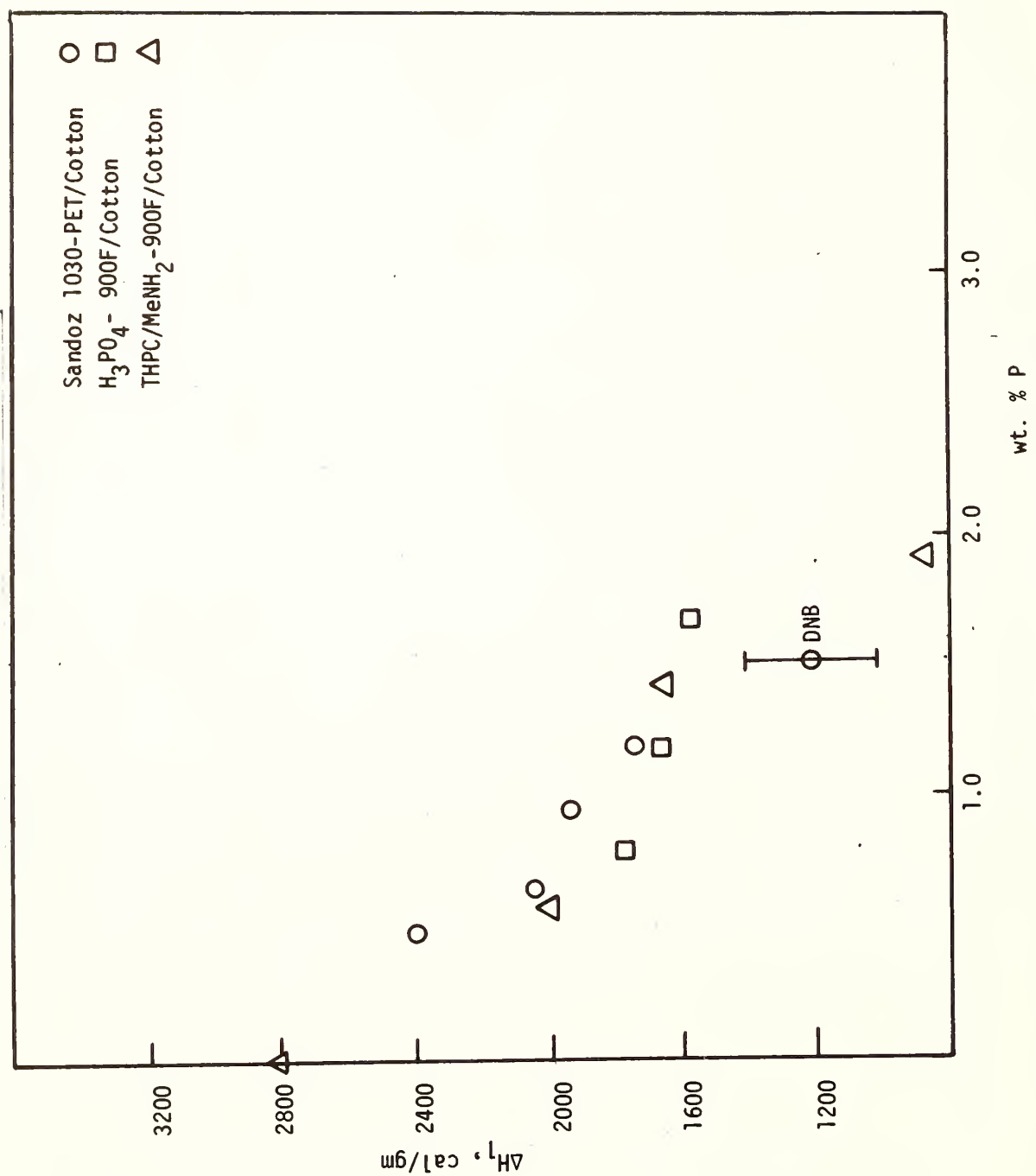


FIGURE 116. Heat release of Sandoz 1030 as a function of wt. %P.

5. Systems Amenable to Fixation by Irradiation

Some preliminary screening experiments were run at Hooker to determine which of the six previously described, specially synthesized monomers could be effectively homopolymerized on the 50 cotton/50 polyester ETIP standard fabric. Free radical polymerization of monomer was initiated in air on fabric by electron beam radiation. Also used were thermal and photochemical decomposition of 2-azo-bis-isobutyronitrile (AIBN) in both air and nitrogen atmospheres.

Fixation of N-(dimethylphosphonomethyl)acrylamide (NDPA) and dimethylphosphonomethyl acrylate (DPA) was observed in these experiments. The other monomers failed to homopolymerize under these conditions. Table CXI shows data obtained with NDPA and DPA using electron beam radiation and photochemical decomposition of AIBN in a nitrogen atmosphere. These data show that higher electron beam radiation doses result in higher fixation efficiencies for both NDPA and DPA; fixation of NDPA is more efficient than DPA at the 24 Mrad dose level; fixation of DPA is more efficient than NDPA with photochemical decomposition of AIBN in a nitrogen atmosphere; and wash durability is excellent for NDPA and DPA derived finishes which were fixed by electron beam radiation.

It should be noted that untreated blend fabric after 50 washes in high phosphate detergent analyzes for about $0.4 \pm 0.1\%$ phosphorus using an X-ray method. This may be a result of inorganic phosphorus residues derived from the detergent, or it may result from interference by calcium that is present in mineral deposits which accumulate during washing in hard water, or possibly a combination of these two factors. Accordingly, it is probably justifiable to think of the phosphorus values at 50 washes as being inflated by this amount.

Not shown in Table CXI are results from the other three conditions under which AIBN was decomposed. Its photochemical decomposition in air resulted in no fixation with any monomer. Thermal AIBN decomposition in air resulted in no apparent fixation of DPA but the highly polymerizable NDPA was fixed in an estimated efficiency of 22% based

ELECTRON BEAM FIXATION OF P AND Br CONTAINING MONOMERS

Phosphorus Analysis

394

TABLE CX1

Cont.

ELECTRON BEAM FIXATION OF P AND Br CONTAINING MONOMERS

Bromine Analysis							
Fabric	Atmo	Br monomer	P monomer	% Applied Br	% Initial	% 50 HW	$\Delta\%$ Br
H	Air	TBPA	None	6.9	2.0	1.6	-0.4
"	"	"	NDPA	7.5	3.0	1.3	-1.7
"	"	"	DMVP	7.9	2.0	1.6	-0.4
"	"	"	DAVP	8.1	1.8	1.1	-0.7
"	"	"	DPA	7.8	1.7	1.2	-0.5
"	"	"	DVP	8.1	2.2	1.5	-0.7
"	"	"	DMAP (R) 76	7.9	2.3	-	-
"	"	"	Fyrol (R) 76	7.8	2.0	1.6	-0.4
H	Air	TBPM	None	6.6	1.7	1.4	-0.3
"	"	"	NDPA	8.1	2.2	1.0	-1.2
"	"	"	DMVP	7.2	1.8	0.9	-0.4
"	"	"	DAVP	7.0	1.3	1.1	-0.2
"	"	"	DPA	8.2	1.9	1.3	-0.6
"	"	"	DVP	7.5	2.1	1.7	-0.4
"	"	"	DMAP (R) 76	7.4	1.6	1.1	-0.5
"	"	"	Fyrol (R) 76	7.2	1.5	0.9	-0.6
E	N ₂	TBPA	None	-	1.0	0.9	-0.1
"	"	"	NDPA	-	2.0	0.7	-1.3
"	"	"	DMVP	-	0.8	0.6	-0.2
"	"	"	DAVP	-	1.1	0.9	-0.2
"	"	"	DPA	-	2.0	1.1	-0.9
"	"	"	DVP	-	1.8	1.0	-0.8
"	"	"	DMAP (R) 76	-	1.7	1.3	-0.4
"	"	"	Fyrol (R) 76	-	2.3	1.4	-0.9
E	N ₂	TBPM	None	-	1.2	0.9	-0.3
"	"	"	NDPA	-	2.0	1.4	-0.6
"	"	"	DMVP	-	1.2	0.8	-0.4
"	"	"	DAVP	-	1.2	0.8	-0.4
"	"	"	DPA	-	1.6	1.0	-0.6
"	"	"	DVP	-	1.9	1.1	-0.8
"	"	"	DMAP (R) 76	-	1.8	1.1	-0.7
"	"	"	Fyrol (R) 76	-	1.2	1.4	+0.2

(1) Hooker Chemicals and Plastics Corp. 50/50 PET/Cotton Fabric

(2) ETIP 50/50 PET/Cotton Fabric

on weight gain. Thermal decomposition in a nitrogen atmosphere resulted in some fixation of the two most polymerizable monomers. Crude calculations based on weight gain give efficiency estimates for NDPA and DPA of 37% and 58% respectively.

Samples prepared by AIBN photochemical decomposition in nitrogen atmosphere were treated by the AATCC vertical flame test using 3 second ignition. After one wash, the specimen treated with NDPA (2.5% P) gave a char length of 2.4 inches, while that treated with DPA (3.0% P) burned the entire length even though it had a higher phosphorus content. These fragmentary data suggested that the finish derived from NDPA might be more effective as a flame retardant than that from DPA.

Combinations of phosphorus and bromine containing monomers were also examined. Electron beam radiation (6 Mrad dose) was used to initiate polymerization of phosphorus (60%) and bromine (40%) monomer combinations on blend fabrics in both nitrogen and air atmospheres. The phosphorus monomers were then prepared by Hooker along with Fyrol 76[®]. Bromine containing monomers used were 2,4,6-tribromophenyl acrylate (TBPA) and 2,4,6-tribromophenyl methacrylate (TBPM).

Base on the data obtained (Table CXI), the following observations were made:

- Efficiency of bromine monomer fixation is poor under all conditions.
- Bromine monomers alone are fixed more efficiently in air than in N₂.
- Fixation efficiencies for NDPA, DPA, and Fyrol 76[®] are generally better in N₂ than in air atmosphere.
- Fixation of the other four phosphorus monomers is poor or nonexistent in all cases.
- For samples irradiated in air, NDPA was fixed more efficiently than Fyrol 76[®].
- Fixation of DPA was inefficient in air but slightly better in nitrogen.

- No treated sample retained more than 1.7% bromine through 50 washes.
- All samples after 50 washes burned completely in the vertical strip test except two which burned along one edge. These two were treated in a N_2 atmosphere with TBPA in conjunction with NDPA and Fyrol 76[®].

A concurrent investigation of flame retardant grafting into polyester/cotton blends was carried out at the Research Triangle Institute. Initial work with the blends used a ^{60}Co source since this was the source used in the previously described work on 100% PET. Experiments with 100% PET and 100% cotton fabric had indicated that the basic techniques developed for PET fibers could be adopted to fabrics and presumably directly to blends. However, model studies with VBr and dimethylphosphonomethyl acrylate (DPA) showed that some modification of conditions and methodology to allow for the cotton would probably be needed to optimize the treatments. For example, in one set of experiments using fabric samples and the mutual irradiation technique developed for PET fibers, VBr was found to produce a grafted add-on of 26% as compared to 9% for cotton fabric treated in the same way. Similarly DPA grafted to add-ons of 7% on PET and 3% on cotton.

These differences were reflected in a lower grafting efficiency on 50/50 blend fabric. Initial grafting trials using the same technique led to add-ons of 9% for VBr, 2% for DPA, 13% for Fyrol BB and 12% for 2,3-dibromopropyl acrylate (DBPA). In an attempt to increase these efficiencies, a brief study was undertaken with the cotton portion of the blend. As in the earlier work, VBr was used as a model. It was found that by using a methanol preswell and a base to act as a scavenger for any acids produced during the process, the VBr could be grafted to cotton fabrics with add-ons up to 150%. Some typical OI data for these fabrics is given in Table CXII.

Elemental analyses of more than 70 different grafted materials for % halogen, or % phosphorus, or % nitrogen or various combinations

TABLE CXII
FLAMMABILITY OF COTTON FABRICS GRAFTED WITH VINYL BROMIDE

<u>% Add-on</u>	<u>OI</u>
0	18.1
26	30.9
43	36.6
118	46.2*
150	63.8*

*These samples did not burn when ignited with a propane/air torch in ambient atmosphere.

of the above three elements revealed that while the % halogen and % nitrogen analyses agreed with the add-on data in general, the % phosphorus was usually low. These analyses were performed by a gravimetric molybdate procedure which is usually presumed to be trouble free for most materials; however, a colorimetric determination for phosphorus has also been used and here various interferences are possible.

With these studies as a background, investigations were then begun on the use of electron beam irradiation in lieu of the ^{60}Co source. Since electron beam methodology seemed to be much more compatible with the demands of commercial textile production all subsequent work was done with sources of this or related types. As a result of the advice and generous cooperation that Processor William K. Walsh of the School of Textiles of North Carolina State University and Professor Vivian Stannett, Vice Provost and Dean of Graduate School, North Carolina State University, have extended to us, the experiments with the accelerated electron grafting were successful from the first experiment.

Because the preceeding studies seemed to indicate that better results might be obtained in most systems if penetration of both the cotton and the PET were achieved, grafting conditions were chosen which should favor diffusion of the retardants into both fibers.

Briefly, the irradiation equipment and the grafting technique consisted of the following. The electron accelerator was a High Voltage Engineering Corporation product with a maximum beam current of 20 milliamps. It was operated at 500,000 electron volts (from an insulated core transformer) for all experiments. This equipment utilizes a horizontal beam scanned to 48" by approximately 6". The samples are hung vertically on a conveyer, which carries them in front of the beam twice in each pass through the equipment so that the samples received half of their total dose from each side. All irradiations were carried out in nitrogen-filled Ziploc[®] polyethylene bags. The beam current and conveyer speed were varied from 0-20 milliamps and 12-96 ft/min. respectively. The dose obtained with these variations was a linear function of the ratio of beam current to conveyer speed as previously established by Professor W. K. Walsh.

The sample (6x6 in.) preparation consisted of drying the fabric in a vacuum oven at 70°C/ 16 hours and then weighing. Next, the samples were preswollen in methanol (1-2 hrs at 40°C-50°C) followed by swelling (1-2 hrs at 50°C-60°C) in a 50% ethylene dichloride solution of the various monomers. The monomer solution also contained 2-4% morpholine as an acid trap and 1-5% of the bis-acrylate of 2-hydroxyethylether of tetrabromobisphenol-A (BABA-50) as a crosslinking agent. Following the swelling procedure the samples were removed from the solution and placed in the polyethylene bags under nitrogen, weighed and then irradiated. The work-up of the irradiated samples was similar to that described before for the fibers.

The electron beam grafting results are given in Tables CXIII, CXIV, and CXV. The following monomers grafted with exceptional ease: N-(dimethylphosphonomethyl) acrylamide (NDPA), bis(2,3-dibromopropyl) phosphonyl-2-oxyethyl methacrylate (BDPOM), DBPA, and BABA-50. Incorporation of NDPA in a formulation as a comonomer facilitated the grafting of monomers otherwise difficult to graft, see Table CXVI.

The NDPA/BDPOM copolymer graft was evaluated in depth since it appeared to be one of the more promising systems producing a sample with an OI=27 at only a 10% add-on when applied to preswollen fabric. The TGA data in Figures 117 and 118 show little evidence for significant grafting of the copolymer on the PET component in the blend fabric but do show a considerable effect on the cotton component. There may be a concentration of NDPA on the cotton and BDPOM on the PET but this could not be determined with certainty. However, it was clear that this system produced an efficient flame retardant effect by the action of P and N on cotton and P and Br on PET.

It was also clear in many of these studies with a variety of monomers, that the effect of preswelling was quite pronounced in terms of both grafting efficiency and flame retardant efficiency. Since the time required for this preswelling would not be compatible with commercial application procedures, it was necessary to develop techniques not involving the utilization of such pre-treatment. As seen with the NDPA copolymer system, application from solution without pre-swelling produced higher add-ons of polymerized material but lowered

TABLE CXIII

ELECTRON BEAM GRAFTING RESULTS

Monomer 50%
 Morpholine 2-4%
 BABA-50 0-3%
 DCE 50%

Preswell in methanol (at 50°C) then monomer solution (at 60°C).

Monomer	Total Dose Mrads	% Add-on	OI
----- Fyrol [®] BB	-- 2 4 8 16	-- 6 6 7.5 7.3	18.5 24.0 24.3 25.2 24.3
DAVP/ZnCl ₂	2 4 8	5 5 6	20.4 20.8 21.4
VBr ₂	2 4 8 16	4 5 5.5 5	22.7 22.7 23.3 22.7
H ₆	4 10 16	(~0) (~1) 3	21.9 21.9 21.9
BABA-50	0.25 0.50 1.00	19 24 (21)	21.9 24.0 24.3
PCPM	2 4 8	2 2 3	19.6 20.0 20.0
DBPM	2 4 8	6 7 10	22.2 23.0 23.5
DBPA	2 4 8	49 51 66	27.1 27.9 29.0
BDPOM	0.50 1 2 4	8 13 33 61	24.3 26.0 30.5 33.1
NDPA	0.50 1 2	59 71 78	32.8 33.7 34.4

TABLE CXIV
ELECTRON BEAM GRAFTING RESULTS

NDPA COPOLYMERS

Preswell in methanol (at 50°C) then monomer solution (at 60°C).

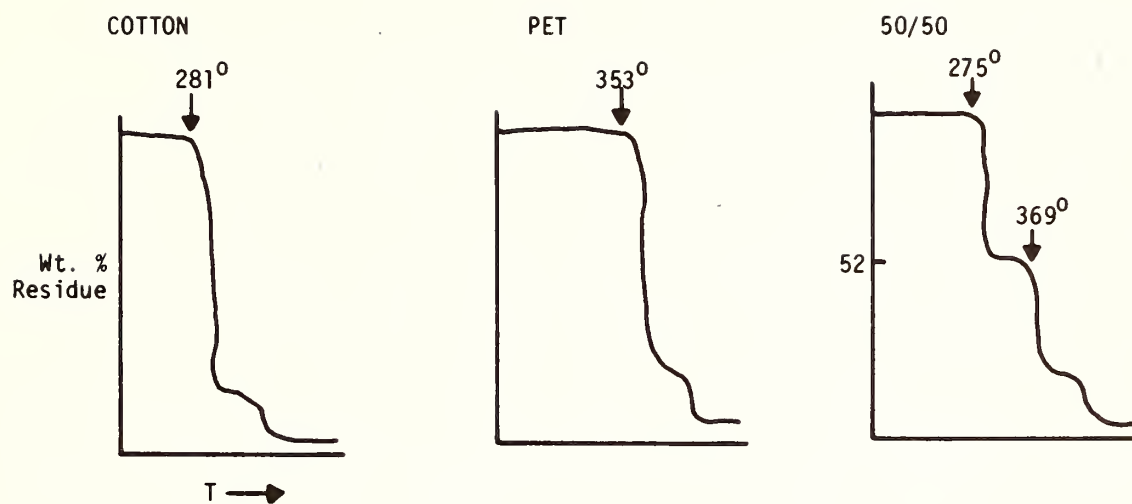
Composition	Total Dose Mrads	% Add-on	OI
NDPA/H ₆	0.25	9	26.3
	0.50	13	27.9
	1.00	18	28.3
NDPA/TBPM	0.25	9	25.2
	0.50	9	26.3
	1.00	11	26.3
NDPA/BDPOM	0.25	10	27.1
	0.50	12	28.6
	1.00	15	28.6
NDPA/DBPA	0.25	22	31.1
	0.50	39	32.5
	1.00	54	34.6
NDPA/Fyrol [®] BB	0.25	32	32.8
	0.50	41	33.5
	1.00	54	33.5
NDPA/BABA-50	0.25	60	31.8
	0.50	81	32.5
	1.00	90	35.4

TABLE CXV
ELECTRON BEAM GRAFTING OF NDPA COPOLYMERS WITHOUT PRESWELLING

Composition	Total Dose Mrads	% Add-on	OI
NDPA/H ₆	0.5	7	22.7
	1.0	16	24.3
	2.0	17	27.1
NDPA/TBPM	0.5	23	28.6
	1.0	43	30.5
	2.0	48	31.4
NDPA/BABA-50	0.5	40	26.0
	1.0	44	29.4
	2.0	47	30.9
NDPA/Fyrol [®] BB	0.5	49	30.5
	1.0	63	32.1
	2.0	(51)	32.5
NDPA/BDPOM	0.5	37	32.1
	1.0	56	34.1
	2.0	66	34.6
NDPA/DBPA	0.5	68	32.8
	1.0	79	35.0
	2.0	93	36.6

TABLE CXVI
EFFECT OF NDPA ON COPOLYMERIZABILITY OF MONOMERS

Flame Retardant	Total Dose (Mrads)	Add-on	OI
Fyrol [®] BB	8	8%	25.2
Fyrol [®] BB/NDPA 50/50 (wt./wt.)	0.25	32%	32.8
Hexa	16	2%	21.9
Hexa/NDPA 50/50 (wt./wt.)	0.50	13%	28.3



NDPA: BDPOM (1:1 by Wt)

no preswell
add on 37%
OI 32.1

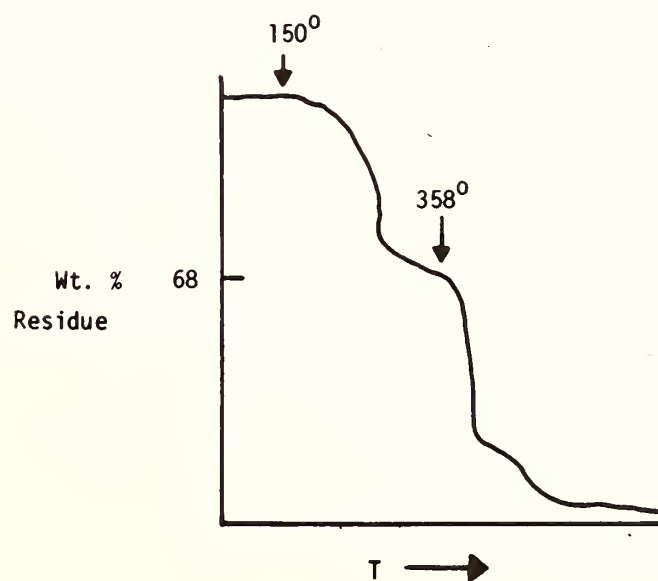


FIGURE 117. Effect of NDPA:BDPOM copolymer grafts of 50/50 PET/cotton TGA.

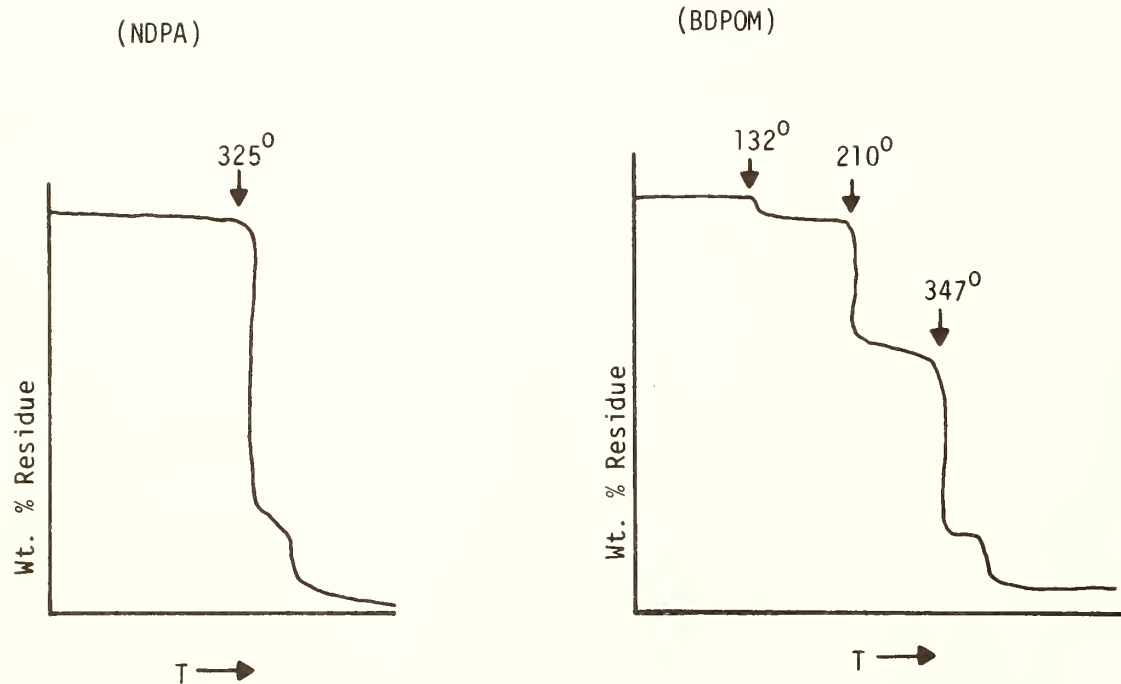


FIGURE 118. TGA data on NDPA and BDPOM homopolymer grafts on 50/50 PET/cotton.

their flame retardant efficiencies (see Table CXVII). This was presumably due to the deposition of much of the flame retardant on the surface of the polyester where it would be more subject to rapid bromine loss during burning and thus have a tendency to lose much of the inhibitor species prior to the flame front.

Although these effects were significant they did not seem to be of such a magnitude as to preclude utilization of direct application procedures without preswelling. Thus, a series of experiments using DBPA in combination with three different phosphorus monomers were carried out. The treated 50/50 blend fabrics were prepared at Clemson and irradiated with a dose of 1.5 Mrads using the electron beam equipment at Deering Milliken Research Corporation. Evaluation by OI gave the results listed in Table CXVIII. Although the data are quite limited, and there is considerable scatter in the results, it appears that the most efficient phosphorus source for this system is the NDPA.

A parallel series of experiments was carried out at RTI using emulsions of the flame retardant monomers rather than solutions. After padding with the emulsions, the fabrics were subjected to heating at 170°C for two minutes and then to irradiation in an electron accelerator. The results of these experiments are shown in Table CXIX. In all cases the phosphorus compound used with NDPA in a 1:1 weight ratio of the bromine containing retardants. The data showed considerable scatter which was probably due to volatilization of some of the bromine-containing monomer from the fabric during drying, but in general, this technique was found to result in an adequate level of add-on and encouraging OI values.

Scanning electron - X-ray microprobe analysis of the graft from an emulsion of NDPA and TBPM on 50/50 PET/Cotton blend fabrics showed that it was possible to graft NDPA not only to cotton but also PET. Some of the data are recorded in Table CXX. More detailed analysis showed that there was a minimal, if any, copolymer formation between the NDPA and TBPM.

Preliminary experiments indicated that the durability of the grafted samples prepared using the emulsions might be a function of both the application procedure and the grafting conditions. For this

TABLE CXVII

EFFECT OF PRESWELLING ON GRAFTING AND FLAME RETARDANT EFFICIENCIES

Composition	Total Dose Mrad	% Add-on Preswollen	% Add-on without preswelling	0.I. preswollen	0.I. without preswelling
NDPA/DBPA	0.50	38.63	67.55	32.5	32.8
NDPA/DBPA	1.00	53.76	79.34	34.6	35.0
NDPA/BB	0.50	41.02	48.92	33.5	30.5
NDPA/BB	1.00	54.35	63.35	33.5	32.1
NDPA/H ₆	0.50	12.57	7.40	27.9	22.7
NDPA/H ₆	1.00	18.22	16.29	28.3	24.3

TABLE CXVIII
ELECTRON BEAM GRAFTING OF PHOSPHORUS MONOMERS WITH DBPA

P. Compd.	P:Br Ratio	% Add-on	%P	%Br	OI	$\frac{OI-17.5}{\% AO}$	$\frac{\Delta OI}{\Delta AO}$
NDPA	2:1	11.48	1.23	2.25	23.25	0.50	0.23
	2:1	17.03	1.82	3.34	24.50	0.41	
	1:1	9.02	0.72	2.65	22.25	0.53	0.72
	1:1	12.13	0.97	3.57	24.50	0.58	
	1:2	6.68	0.36	2.62	22.00	0.67	0.66
	1:2	8.20	0.44	3.21	23.00	0.67	
DPA	2:1	18.39	1.96	3.61	22.75	0.29	0.10
	2:1	8.76	0.93	1.72	21.75	0.49	
	1:1	5.37	0.43	1.58	21.25	0.69	0.16
	1:1	14.46	1.16	4.25	22.75	0.36	
	1:2	5.92	0.32	2.32	21.25	0.63	0.33
	1:2	8.18	0.44	3.21	22.00	0.55	
Fyrol [®] 76	2:1	6.56	0.98	1.29	20.75	0.50	
	1:1	10.01	1.12	2.94	23.50	0.60	
	1:2	8.03	0.60	3.15	22.25	0.59	

TABLE CXIX
GRAFTING USING MONOMER EMULSIONS

Sample	Total Dose (Mrads)	% Add-on	OI
1. NDPA/DBPA	0.25	17.2	27.6
2. NDPA/DBPA	0.50	28.6	29.4
3. NDPA/DBPA	1.00	21.2	30.1
4. NDPA/BDPOM	0.25	11.9	26.3
5. NDPA/BDPOM	0.50	18.0	26.7
6. NDPA/BDPOM	1.00	16.7	26.7
7. NDPA/BB	0.25	19.4	28.3
8. NDPA/BB	0.50	22.3	28.6
9. NDPA/BB	1.00	15.5	28.3
10. NDPA/TBPM	0.25	18.4	26.7
11. NDPA/TBPM	0.50	29.2	28.3
12. NDPA/TBPM	1.00	32.4	29.4

TABLE CXX

SEM X-RAY MICROPROBE ANALYSIS OF 50/50 BLEND
GRAFTED WITH NDPA/TBPM

<u>Fiber</u>	<u>% Add-on</u>	<u>OI</u>	<u>Viewing Mode</u>	<u>P/Br Analysis</u>
Cotton	0	18.1	-	-
	130	43.1	Longitudinal	P>>Br
	130	43.1	cross sectional	P>>Br
Polyester	0	25.2	-	-
	17	26.3	Longitudinal	P=Br
	17	26.3	cross sectional	P>Br

reason, the durability has been studied in considerable detail. Most of the samples were laundered for 25 cycles. The samples were washed according to AATCC Test Method 124-1967 in a Sears Kenmore® 600 washer, normal cycle, low water level, with a 3 lb dummy load and the water at approximately 130°F. A 12-minute washing cycle was used with 90 grams of AATCC standard detergent in each cycle. The samples were dried in a closed dryer after the 10th and 25th cycles only and were then evaluated for oxygen index.

One series of samples was prepared by applying the neat monomer mixtures to the fabrics prior to irradiation. The results of these are listed in Table CXXI. All of the samples except the NDPA/BABA 50 showed a significant problem with durability. In most cases, the first 10 cycles were effective in removing a significant portion of the flame retardant. Beyond this there appeared to be little change through 25 cycles.

A second set of samples was prepared from a 50% aqueous monomer emulsion and irradiated in a nitrogen atmosphere. The results obtained with these samples are given in Table CXXII. As can be seen, these samples exhibited significantly higher durability than those prepared using neat monomer application. Similar results were obtained on samples padded from emulsion but irradiated in an air atmosphere (Table CXXIII). This is particularly significant in terms of the applicability of these treatments in commercial processes.

The effect of application and fixation conditions are compared in Table CXXIV. On the basis of these results there would seem to be little reason to expend extra effort to protect the fabric from air during irradiation. These results also indicate that application from aqueous emulsion should be easier to control although the application of the neat monomers should be feasible using printing methods or other techniques to moderate the add-ons.

Other application parameters were also studied. Because of the reduced retardant efficiency observed when the methanol preswelling was omitted from the application procedure, attempts were made to find an acceptable alternate pre-treatment method which would result in

TABLE CXXI
DURABILITY OF FABRICS GRAFTED USING NEAT MONOMER MIXTURES

Composition/Total Dose	% Add on	OI Before Washing	OI After 2 Cycles	OI After 10 Cycles	OI After 25 Cycles
NDPA/H ₆ /0.5 Mrads	8	22.7	28.6	21.4	----
1	16	24.3	30.1	22.7	----
2	17	27.1	30.5	23.5	----
NDPA/TBPM/0.5	23	28.6	29.0	22.2	22.2
1	43	30.5	30.1	23.3	22.7
2	49	31.4	31.4	24.7	24.3
NDPA/BABA/0.5	40	26.0	28.3	28.6	28.3
1	44	29.4	32.5	31.1	31.1
2	47	30.9	32.5	31.8	31.4
NDPA/Fyrol [®] BB/0.5	49	30.5	24.7	25.5	25.2
1	63	32.1	26.7	26.7	26.3
2	(51)	32.5	28.6	28.3	27.6
NDPA/BDPOM/0.5	37	32.1	33.1	22.7	22.2
1	56	34.1	34.4	23.5	23.5
2	66	34.6	35.6	24.3	24.0
NDPA/DBPA/0.5	68	32.8	34.1	28.3	27.9
1	79	35.0	35.0	31.4	31.4
2	93	36.6	37.8	33.5	31.8

TABLE CXXII

DURABILITY OF FABRICS GRAFTED UNDER N₂ USING MONOMER EMULSIONS

Composition/ Total Dose	% Add-on	OI Before Washing	OI After 10 cycles	OI After 25 cycles
NDPA/DBPA/1	28	29.0	29.0	28.3
60 40 2	26	29.7	29.0	27.9
4	41	29.7	30.1	30.1
NDPA/DBPA/1	28	27.1	27.9	27.1
40 60 2	28	27.9	29.0	28.3
4	25	28.3	29.7	28.6
NDPA/Fyrol [®] BB/1	19	29.0	26.3	26.0
60 40 2	24	29.7	26.7	26.0
4	32	30.5	28.6	27.1
NDPA/Fyrol [®] BB/1	18	28.3	26.3	25.2
40 60 2	13	28.6	26.3	24.7
4	15	28.6	26.3	24.3
NDPA/TBPM/1	25	28.6	28.6	27.6
60 40 2	24	29.0	29.0	27.6
4	25	29.0	29.4	27.9
NDPA/TBPM/1	18	27.6	27.1	26.3
40 60 2	18	27.9	27.9	26.3
4	21	28.3	27.9	26.3
NDPA (50%)/1	37	29.7	27.9	27.1
2	42	30.9	29.0	27.9
4	47	30.9	29.0	28.3

TABLE CXXIII

DURABILITY OF FABRICS GRAFTED IN AIR USING MONOMER EMULSIONS

Composition/ Total Dose	% Add-on	OI Before Washing	OI After 10 cycles	OI After 25 cycles
NDPA/DBPA/1	30	29.0	27.6	29.0
60 40 2	35	28.6	28.6	31.1
4	44	31.1	30.1	31.4
70-30/1	26	29.7	28.3	28.6
2	28	29.4	28.3	29.4
4	37	30.5	29.0	29.0
80-20/1	39	30.9	29.0	29.0
2	56	31.1	29.4	30.1
4	--	33.1	30.5	30.1
NDPA/Fyrol ^(R) BB/DBPA/1	--	31.8	30.1	29.4
50 25 25 2	34	31.8	29.7	29.4
4	31	32.5	29.4	29.0
60-20-20/1	38	28.3	27.9	27.9
2	30	28.6	28.6	29.7
4	35	30.5	29.7	29.4
70-15-15/1	42	31.4	29.4	30.1
2	31	31.8	29.4	30.1
4	32	31.8	30.1	29.7
NDPA/TBPM/1	32	29.7	29.0	29.7
60 40 2	40	30.1	29.0	29.4
4	(68)	30.1	30.1	29.4
70-30/1	36	28.6	29.4	29.0
2	56	29.7	30.1	30.5
4	--	30.9	31.1	30.9
NDPA (25%)/1	19	27.9	26.7	27.6
2	17	26.3	26.7	27.6
4	16	26.3	26.3	26.3

TABLE CXXIV

EFFECT OF GRAFTING PARAMETERS ON DURABILITY

Composition/Total Dose	NEAT, N ₂ -			EMULSION, N ₂ -			EMULSION, AIR		
	% Add-on	OI Before Washing	OI After 25 Cycles	% Add-on	OI Before Washing	OI After 25 Cycles	% Add on	OI Before Washing	OI After 25 Cycles
NDPA/DBPA/0.5	68	32.8	27.9	--	---	---	--	---	---
50 50 1	79	35.0	31.4	28	29.0	28.3	30	29.0	29.0
60 40* 2	93	36.6	31.8	26	29.7	27.9	35	28.6	31.1
4	--	----	----	41	29.7	30.1	44	31.1	31.4
NDPA/TBPM/0.5	23	28.6	22.2	--	---	---	--	---	---
50 50 1	43	30.5	22.7	25	28.6	27.6	32	29.7	29.7
60 40* 2	49	31.4	24.3	24	29.0	27.6	40	30.1	29.4
4	--	----	----	25	29.0	27.9	(68)	30.1	29.4
NDPA/Fyrol [®] BB/0.5	49	30.5	25.2	--	---	---	--	---	---
50 50 1	63	32.1	26.3	19	29.0	26.0	--	---	---
60 40* 2	(51)	32.5	27.6	24	29.7	26.0	--	---	---
4	--	----	----	32	30.5	27.1	--	---	---
NDPA/1	--	----	----	37	29.7	27.1	19	27.9	27.6
2	--	----	----	42	30.9	27.9	17	26.3	27.6
4	--	----	----	47	30.9	28.3	16	26.3	26.3

higher efficiency of the grafted flame retardant but still be compatible with commercial processing requirements. One of these which looks particularly promising is based on the use of liquid methylamine. This seemed to result in both an increase in the flame retardant efficiency as measured by OI, and a slight increase in the flame retardant add-on. The effect is most pronounced in the case of 100% cotton, presumably because of methylamine's ability to de-crystallize cellulose. An example of this effect can be seen in the data presented in Table CXXV.

The effect of varying the nature of the source was also studied. A significant reduction had been noted in changing from ^{60}Co to the scanned electron beam (see Table CXXVI for typical data). This, however, may be dependent to some degree on the structure of the monomers since Fyrol BB seems to exhibit essentially the same grafting efficiency with both radiation sources. More importantly, the NDPA systems seem to graft more efficiently in the lower energy sources. Such effects could be very important, particularly if the flame retardant systems developed with one radiation source are to be applied using a different source. As an example, there is considerable interest in the textile industry in the Electrocurtain[®] processor developed by Energy Sciences, Inc. This equipment operates at lower energy than the scanned electron beam source. Thus attempts have been made to evaluate some of the copolymer graft treatments using the Electrocurtain[®]. Typical results are presented in Tables CXXVII and CXXVIII. These results are encouraging but indicate the need for additional studies to optimize the application and fixation techniques.

In an alternate approach to the application problem, experiments were carried out to determine the feasibility of applying the monomers by conventional drying techniques. Samples of NDPA, DBPA and TBPOEA (tribromophenoxyethyl acrylate) were applied to cotton fabric using procedures for the application of direct dyes but none of the three were found to exhibit any significant affinity and thus only very low pick-ups were achieved. The TBPEOA was used in these studies in place of the TBPM since it contained similar bromine functionality but

TABLE CXXV

EFFECT OF METHYLAMINE PRETREATMENT ON NDPA/DBPA GRAFTING AND FLAME RETARDANCE

Sample	Total Dose (Mrads)	No Pre-Treatment		MeNH ₂ Pre-Treatment	
		% Add-on	OI	% Add-on	OI
100% Cotton	0.25			93.5	40.6
	0.50			87.0	46.2
	1.0			83.8	49.0
100% Polyester	0.25	31	28.6	25.8	30.5
	0.50	39	28.6	32.9	32.1
	1.0	45	29.0	31.1	34.4
50/50 PET/Cotton	0.25			65.3	34.6
	0.50	68	32.8	81.2	40.6
	1.0	79	35.0	76.8	42.7
	2.0	93	36.6		

TABLE CXXVI
COMPARISON OF GRAFTING SOURCES

<u>MONOMER COMPOSITION</u>	<u>SOURCE</u>	<u>DOSE(Mrads)</u>	<u>%ADD-ON</u>	<u>OI</u>
Fyrol ^(R) BB 2% BABA-50	γ	1.95	6	-
	γ	4.3	7	-
	γ	7.95	9	-
	e ⁻ beam	2	6	-
	e ⁻ beam	4	6	-
	e ⁻ beam	8	7.5	-
DAVP/ZnCl ₂ 2% BABA-50	γ	1.95	8	-
	γ	4.3	9	-
	γ	7.95	10	-
	e ⁻ beam	2	0	-
	e ⁻ beam	4	0	-
	e ⁻ beam	8	0.4	-
BABA-50		0.7	45	-
	e ⁻ beam	1	3	-
NDPA ⁽¹⁾	γ	1	0	20.4
	γ	5	3	20.8
	e ⁻ beam	1	19	27.9
	e ⁻ beam	4	16	26.3
	e ⁻ curtain	1	6	24.7
	e ⁻ curtain	5	10	25.5
NDPA/Fyrol ^(R) BB ⁽²⁾ 55 45	γ	1	3	22.7
	γ	5	10	25.5
	e ⁻ beam	1	19	29.0
	e ⁻ beam	4	32	30.5
	e ⁻ curtain	1	12	26.3
	e ⁻ curtain	5	19	28.6

(1) Solution

(2) Emulsion

TABLE CXXVII
SELECTED FORMULATION FOR e⁻ CURTAIN EXPERIMENTS

Formulations

NDPA - 33% H₂O solution

NDPA/DBPA - 50% H₂O emulsion, 4% Triton X-100^(R)
 40 60

NDPA/DBPA/TBPM - 43% H₂O /DCE emulsion, 3% Triton X-100^(R)
 40 30 30 3.3 1

NDPA/DBPA/Fyrol^(R) BB- 50% H₂O emulsion, 4% Triton X-100^(R)
 40 30 30

Sample Size - 18 in. x 72 in.

Wet add on - 120 - 160%

Predrying - 94⁰C (200⁰F), 7 mins., forced air

NDPA/DBPA

NDPA/DBPA/TBPM

NDPA/DBPA/Fyrol^(R) BB

Total Dose - 1 Mrad and 5 Mrads

Atmosphere - essentially ambient air

TABLE CXXVIII

DURABILITY OF SAMPLES GRAFTED IN AN e^- CURTAIN

<u>Sample/Total Dose</u>	<u>% Add on</u>	<u>OI After 1 Washing</u>	<u>OI After 10 Washing</u>
Ungrafted - 1	--	18.5	----
- 5	--	19.2	----
NDPA - 1	6	24.7	24.3
- 5	10	25.5	25.5
NDPA/DBPA - 1	11	25.5	24.7
- 5	17	26.3	26.3
NDPA/DBPA/TBPM - 1	8	24.3	22.2
- 5	11	25.5	23.5
NDPA/DBPA/BB - 1	12	26.3	26.0
- 5	19	28.6	27.6

appeared to be more readily available on a commercial scale.

Similarly, application of the retardants to polyester was attempted using disperse dye procedures with and without carriers. Considerably better results were obtained in these experiments as shown in Table CXXIX. These samples were fixed by irradiation using the Electrocurtain[®].

Attempts to use this same approach for the treatment of 50/50 blends was less successful as shown by the data in Table CXXX. Only the TBPOEA appeared to be a good candidate for dyebath application. All dyeings were carried out in the presence of both carrier and NaCl in an attempt to maximum exhaustion into both fibers. Although the TBPOEA appeared to exhaust almost completely onto both 100% PET and the 50/50 blend, examination of the treated fabrics indicated that very little of the retardant had penetrated the fibers and most of it was present as a coating on the fabric. This caused significant problems upon attempts at further processing. Attempts to pad an NDPA solution onto the TBPOEA treated fabric followed by radiation curing led to a finish with poor flame retardant efficiency due to the inability of the NDPA to penetrate the TBPOEA coated fibers. Attempts to apply the NDPA prior to the TBPOEA dyeing failed because of the extraction of the NDPA from the fabric if previously unfixed and degradation during high pressure dyeing of the NDPA treated fabric when previously fixed. Efforts to apply the two monomers together in a padding operation also failed because of the difficulties encountered in trying to prepare a stable pad bath with a sufficiently high concentration of TBPOEA.

In still a different approach to the application and fixation problems the reactive bromine containing monomers were replaced by the essentially inert and insoluble decabromodiphenyl oxide in the form of the commercial FR P-53[®] system. The NDPA was then cured using the scanned electron beam to give an apparently durable finish in which the NDPA acts as the binder for the P-53. The results of these preliminary experiments are given in Table CXXI. Unfortunately these data give little information about the effectiveness of the finish since the fixation was much better than expected and thus the add-on levels were extremely high.

TABLE CXXIX
DYEBATH APPLICATION OF FLAME RETARDANTS TO PET

<u>Monomer</u>	<u>Carrier</u>	<u>% Add-on</u>
NDPA	benzene	2.6
NDPA	none	0.9
DBPA	benzene	9.3
DBPA	none	8.4
TBPOEA	benzene	17.6

All samples dyed 2 hours @ 100°C, extracted, dried subjected to 5 Mrad irradiation, and washed.

TABLE CXXX

DYEBATH APPLICATION OF FR MONOMERS TO 50/50 BLENDS

<u>Monomer</u>	<u>% Add-on</u>
NDPA	0.8
DBPA	2.7
TBPOEA	3.8

TABLE CXXXI
DURABILITY OF FR P-53^(R) USING GRAFTED NDPA AS A BINDER

Sample/Total Dose mrad	% Add on	OI Before Washing	OI After 10 cycles	OI After 25 cycles
NDPA/P-53 ^(R) /1	84	30.9	29.7	29.4
60 40 2	89	31.8	30.1	29.0
4	128	32.8	32.1	29.7
50/50/1	76	30.9	30.5	29.7
2	78	32.1	30.9	30.1
4	104	32.5	31.1	30.1
40/60/1	55	32.1	29.7	29.7
2	52	32.1	30.5	30.1
4	58	32.5	30.9	29.7

SUMMARY AND CONCLUSIONS

The overall goal of this project was to develop one or more commercially feasible flame retardants for polyester/cotton blend fabrics, while at the same time demonstrating that such a project could be successfully carried out by a consortium of research teams with widely varying interests. This consortium included teams from three academic institutions, one government laboratory, a fiber manufacturer, a textile manufacturer, and two chemical companies. The project was also administered in such a way as to maximize the input from other laboratories not directly involved in the consortium.

The target fabric chosen for this work was a 4.2 ounce per square yard 50/50 polyester/cotton poplin. This fabric was chosen on the basis of its weight and construction which should represent a maximum challenge for a new flame retardant finish. It was felt that finishes which could be successful on this fabric should be broadly applicable to a wide range of other weights and constructions.

The project was approached with no preconceptions of the most desirable types of flame retardant systems or application procedures. In fact, considerable emphasis was placed on developing finishes which might be applied by non-conventional processes such as radiation grafting.

Since the textile literature contained a considerable body of information concerning the theory and practice of flame retardant finishing of cotton but relatively little regarding polyester, much of the initial effort was devoted to developing an understanding of the flammability and flame retardation of polyester and the interactions which occur between burning polyester and cellulose in blends. An indepth study was made of the normal variables which might be encountered in dealing with polyesters and the effects which these variables might have on the fiber's flammability. A series of polyesters was prepared with varying concentrations of catalysts, diethylene glycol, free carboxyl, and carbomethoxy. These were evaluated by both oxygen index and thermal analysis. Although there did appear to be some effect on both the flammability and thermal behavior as a function of these variables, there was no evidence of the types of effects which should

significantly alter the flammability of either the polyester alone or in blends when evaluated in a test such as FF 3-71.

The effect of various types of flame retardants on polyester was also studied in detail. Different modes of incorporation of the flame retardants into the polymer were evaluated for samples in which the retardant had been added by topical treatment, melt blending or copolymerization. Again the data seemed to indicate that these variations might have discernable effects on the thermal behavior of the polyester, but none of these was of such a magnitude as to be considered a major factor in the overall flammability of fabrics. It also appeared that these effects would be further diminished by placing the polyester in a blend environment.

In addition to the oxygen index studies, the efficiencies of both phosphorus and bromine flame retardants on polyester were studied by isoperibol calorimetry. Evaluation of polyester treated with a series of organobromine compounds of various structures and thermal stabilities showed that the previous observations of aromatic bromine as a more efficient retardant than aliphatic bromine could be related to the ability of the aromatics to decrease the heat released by polyester during burning. Concurrent thermal analysis studies showed that the key factor in this increased efficiency was probably the increased thermal stability of the aromatic compounds. It was also demonstrated that while the fragmentation temperature of the organo halogen compounds was important its ability to release hydrogen bromide was not.

Phosphorus compounds were also studied as flame retardants for polyester, but a similar series of efficiency studies was not carried out. However, there was sufficient evidence to indicate that addition of organophosphorus compounds could result in effective flame retardation of the polyester. After screening a large number of compounds it was found that one of the best additive systems was that based on hexaphenoxyposphazene. Developmental quantities of the additive have been obtained and pilot plant evaluation of the material is currently in progress. It is hoped that this will yield a sufficient quantity of inherently flame retardant polyester to allow a complete evaluation

in blends with cotton and rayon. Although this will not be accomplished within the time frame of the ETIP project, arrangements have been made for this work to be continued by several of the industrial members of the consortium after the close of the formal project.

The thermal degradation kinetics of inherently flame retardant polyesters containing tetrabromobisphenol-A (Dacron[®] type 900F) and 10% hexaphenoxyposphazene were studied in both oxidative and inert atmospheres. This showed that oxygen, phosphorus and bromine can all effect the condensed phase reactions of the polyester. On this basis, a non-residue forming, condensed phase flame retardant mechanism was proposed. However, the significance of this mechanism in terms of observable flammability properties of either 100% polyester or polyester/cotton blend fabrics could not be established with the data available.

In addition to these basic studies, an effort was made to determine the practicability of fixing flame retardants onto polyester fibers by radiation grafting techniques using ⁶⁰Co_γ radiation. From these experiments several conclusions can be drawn:

- (1) It appears that the polyester can be rendered flame resistant by grafting techniques. Preswelling appears to increase the grafting efficiency; and the grafting efficiency also seems to be very dependent upon the structure of the monomers in both the phosphorus and bromine series. The physical properties of the grafted fibers do not appear to be altered to a great extent, except for the fiber elongation at break which increases in some instances to twice its original value.
- (2) Copolymer grafts appear in many cases to be more efficient in terms of both fixation and flame resistance than the corresponding homopolymer grafts.
- (3) It appears to be possible to selectively graft polyester fibers on the surface, in the core, or uniformly throughout the PET fiber. Those flame

retardant monomers which are more volatile appear to have an increased efficiency when fixed deep within the fiber matrix.

(4) As expected, the aromatic bromine-containing monomers were found to be more efficient flame retardants than those containing aliphatic bromine, and this efficiency could be related to the thermal stability of the bromine-containing moieties.

Once some understanding of the factors effecting polyester flammability and flame retardants had been achieved, attention was turned to the polyester/cotton blends. The strategy was again to develop an understanding of the factors controlling the flammability and flame retardant action, then using this information to design and evaluate a series of prototype flame retardants. From these results it was hoped that commercially feasible treatments might be developed. This immediately raised the problem of determining commercial feasibility, a particularly difficult task since there were no specified criteria for determining the level of flame resistance necessary for a marketable fabric. Thus, considerable effort was expended on developing and comparing test methodology. A series of blends was evaluated by a variety of techniques including the vertical flame test of FF 3-71, isoperibol and oxygen bomb calorimetry, oxygen index in both the top and bottom ignition modes, heat transfer on the purposed MAFT, subjective evaluation of burning characteristics on a pin frame mounted at a 45° angle, and a determination of fabric ignition characteristics on a specially designed ignition tester. Unfortunately, there did not appear to be a good correlation between any of these tests; so it was necessary to utilize all of them in the subsequent work since it did not appear that any single test provided a reliable measure of fabric flammability for general commercial purposes. The calorimetric methods were used primarily as probes into flame retardant mechanisms. The other tests were used for screening prototype systems with particular emphasis being placed on vertical and 45° angle flame tests with subjective evaluation of burning and ignition characteristics.

Using these methods a detailed investigation was made of the flammability of polyester/cotton blends containing a variety of model flame retardant treatments. The interaction of the fibers in the blends was studied as a function of flame retardant activity on each of the two fibers. A series of phosphorus and bromine containing retardants were examined both individually and in combinations. Isoperibol calorimetry showed that interactions do occur between the fibers in many cases; and in no case was the flammability of a blend found to be a simple sum of the flammability properties of the constituent fibers. Flame retardants such as diammonium phosphate or phosphoric acid, which are generally found to limit their effectiveness to the condensed phase of cellulose, appeared to impart little flame resistance to the polyester. And, in some cases when present in low concentrations, these retardants seemed to lead to an increase in the combustion efficiency of the polyester portion of the blend. The role of other model phosphorus-containing systems was less well defined, but it could be shown that some volatilization of the phosphorus was important in determining the flame resistance of the blend fabric. This led to a study of chemical oligomers of phosphonium compounds such as THPC. Several oligomeric structures were synthesized and characterized by ^1H , ^{31}P , and ^{13}C n.m.r. These systems were then intensively studied by calorimetry. This evaluation indicated that the mode of flame retardant action was very similar for all of the oligomers and it appeared that the controlling factor in determining the flame retardant efficiencies was simply their phosphorus contents. However, there were some very real differences in the aesthetic properties of the fabrics finished with the different oligomer systems. It was observed that better aesthetic properties could be obtained by incorporating methylol carbamates or other difunctional monomers capable of imparting linear structures to the oligomers. This, however, resulted in a dilution of phosphorus content of the retardant with a corresponding decrease in flame retardant efficiency. Conversely, the flame retardant efficiency could be increased by reducing the amount of resin present and utilizing an ammonia cure instead of a heat cure. This, however, led to a

more highly crosslinked structure and poor aesthetic properties. Thus it would seem that it would be necessary to optimize the structures for each specific set of aesthetic and flame retardant criteria.

The flame retardant efficiency of bromine containing retardants on polyester/cotton blends followed the same order as on 100% polyester. Aromatic bromine compounds in the presence of antimony oxide were better than those without the antimony, which in turn were more efficient than the aliphatic bromine systems. These systems also showed a distinct lack of dependence of flame retardant efficiency on the nature of the substrate, indicating that they were probably involved only in fuel consuming processes rather than fuel generating ones.

In order to study the interaction of phosphorus and bromine containing species on the blends, combinations of diammonium phosphate with 2,3-dibromopropylphosphate, tetrabromobisphenol-A (as Dacron[®] type 900F) with phosphoric acid and THPC with polyvinylbromide were subjected to examination. The results indicated that phosphorus and bromine act independently in these systems and a set of generalized response characteristics could be ascertained so that formulations could be optimized based on calorimetric data. In general it seemed that the optimum amount of any condensed phase active phosphorus species on the cellulosic portion was 1½-2% P with enough bromine added to reach the desired level of flame retardancy. For a vertical test such as that in FF 3-71 this would require approximately 6% bromine, or a bromine to phosphorus ratio of approximately 4:1 assuming a reasonable degree of durability. Of course, any lack of durability would have to be compensated for by increasing the bromine content of the finish. Since these parameters were apparently independent of the mode of application they could be use as a guide for the development of more practical treatments.

The other guide lines which were established by the model compound studies were as follows:

- (1) For retardants containing only phosphorus the fundamental unit $P(O)(CH_2)_3$ is the most desirable.

This moiety has a potential for high phosphorus content, good thermal and hydrolytic stability, reasonable effectiveness on the cellulose decomposition, and reaction with a variety of other functional groups. There also seemed to be other basic structural units, such as the phosphazene ring with proper substituents to obtain high thermal and hydrolytic stability, which should work as well as the phosphine oxide function, but an insufficient number of these materials were available for this study. The overall efficiency of these phosphorus retardants is generally quite high but the effectiveness is frequently less than anticipated because of a low phosphorus content in the finishes. Those finishes with higher phosphorus contents generally produce poor aesthetic properties.

(2) For systems containing bromine in the absence of phosphorus the greatest effectiveness is achieved by incorporation of antimony oxide as a co-reactant. Even the more inherently effective aromatic bromine is generally not of sufficiently high efficiency to produce a useful finish in the absence of antimony. With the presence of antimony oxide a bromine content of 7-8% is generally required to pass a vertical test such as FF 3-71. The bromine systems do have an advantage over the phosphorus retardants, however, because of their high bromine content in the final finish. But they also present a number of disadvantages since they frequently have a greater potential for photochemical and physiological reactions and a lower reactivity in fixation processes. Most of the organobromine compounds must be applied with a binder system which decreases their efficiency and frequently causes problems with aesthetic properties. These materials also are often found to have lower durability than compounds such as the

phosphorus oligomers. However, the ETIP group has developed at least one highly effective formulation by utilizing a thermally stable bromine-containing acrylic binder system based on poly(2,3-dibromopropyl acrylate), a material developed by the ETIP team in cooperation with Chas. S. Tanner and Co.. This system also has the advantage that it does not seem to depend on interactions with the fuel generating process and is therefore more generally applicable to a wide variety of fibers and blends.

(3) Phosphorus and bromine can usually be used together with significant advantages. Initial work by the ETIP consortium centered on the THPC/urea/polyvinylbromide system developed at SRRC. It was found that replacement of the polyvinylbromide by a vinyl bromide-vinyl chloride copolymer could alleviate some of the discoloration problems encountered with this finish. But, under mill conditions this system still exhibited some tendency toward discoloration. In an attempt to circumvent this problem, the vinyl bromide-containing latex was replaced by poly(2,3-dibromopropyl acrylate). This material allowed the preparation of samples with THPC/urea which were not noticeably discolored and which could be adjusted to produce good flame retardancy if the bromine content was sufficiently high. The finish could be further improved by replacing the THPC/urea with a phosphonium precondensate to increase the phosphorus content. Unfortunately, all of the fabrics produced in this way, which had the requisite flame retardancy, also had an unacceptably stiff hand. Attempts to modify the stiff hand by the incorporation of silicone softeners led to a deterioration of the flame retardant characteristics of the fabrics. In an alternative approach to the phosphorus-bromine

systems a cooperative project with Sandoz Colors and Chemicals has lead to the development of a system based on a bromine-containing phosphazene which is capable of imparting a high degree of flame resistance with very good durability to a variety of polyester/cotton blend fabrics. When laundered and dried under normal home use conditions these fabrics possess good aesthetic properties. However, when heated to high temperatures, such as those encountered in commercial drying and curing operations, the hand of the fabric is significantly stiffened.

(4) Radiation grafting appears to offer a good long range solution to the problem of polyester/cotton blend flammability. It has the potential for good fixation of the retardants with low energy consumption and should produce fabrics with good flame retardancy and durability. However, there are still many unstudied parameters which prevent its immediate utilization for flame retardant finishing on a general basis throughout the industry.

The ETIP work has thus led to one system which should be feasible to run commercially with only a little work to remove variable durability results {FR P-44[®] with P(DBPA)}, three systems which need further work to remove problems associated with fabric hand {Sandoz 1030, THPS[®]-urea-P(DBPA) and the phosphonium precondensates} and a series of systems with a potential as a long range solution to the flammability problem but which needs considerably more research (radiation grafting of P and Br containing monomers).

From the standpoint of research management, the project has also been quite successful as evidenced by the fact that the members of the ETIP consortium have decided to continue to meet on a quarterly basis for at least one year after the formal termination of the project.

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INDEX

AATCC 25

Acetaldehyde 57-58

Acrylic latices

See: Dur-P-Cryl[®] BL-1

Dur-O-Cryl[®] XWC

Aerotex[®] 23 242, 291, 299

American Cyanamid Co. 23

American Enka 10, 120, 171

American Hoechst Corp. 23

45° angle burning 82, 104, 215, 217, 223, 242-244, 249, 252, 256, 285, 359

Antiblaze[®] 19 83-86, 215-217, 246-248

Antimony oxide 97, 358-359

See: Nyacol

P-44

BABA 50

See: bis-acrylate of 2-hydroxyethyl ether of tetrabromobisphenol A

BDPOM

See: bis(2,3-dibromopropyl)phosphonyl-2-oxyethyl methacrylate

Beaunit Corp. 23

Bisacrylate of 2-hydroxyethyl ether of tetrabromobisphenol A (BABA 50)
400-425

Bis(2,3-dibromopropyl)phosphonyl -2-oxyethyl methacrylate (BDPOM)
400-425

Bromine ion detection 139

Bromoform 76-78, 243

Cav-gard[®] FR R3-39 322

Chargard[®] FR 989 118

Children's sleepwear standard 77, 81-82, 104, 113-120, 174, 208, 212, 253, 256, 285, 290-301, 312, 317, 378, 380-838, 393

Ciba Geigy 23, 75, 271

Citex[®] BT 93 321

Cities Service Co. 23, 322

Clemson Univ 15, 24-25, 219, 268, 356, 378, 407

Commercialization plan 16

Condensed phase oxidation 149

Consortium

- Members 3
- Operation 7

Cyanoacetylpiperidine 376

Dacron[®] 900F 131, 341, 346, 351, 361, 366, 375

See: tetrabromobisphenol A

Dan River, Inc. 23

DAP

See: diammoniumphosphate

DAVP

See: dimethyl 1-acetoxyvinylphosphonate

DBDPO

See: decabromodiphenylene oxide

DBPA

See: 2,3-dibromopropyl acrylate

DBPM

See: 2,3-dibromopropyl methacrylate

Decabromodiphenyl oxide (DBDPO) 97, 100, 130, 134, 304, 308

See: P-44[®]

P-53[®]

Deering Milliken Research Corp. 23, 407

DEVP

See: diethylvinylphosphonate

Diammoniumphosphate (DAP) 38-39, 52, 83-85, 91-92, 97-107, 146,
148, 246-249, 253, 254, 279, 281, 329, 334, 341

6,6-diaminotetrachlorocyclotriphosphazene 244

1,3,2-diazaphosphorinane 242

Dibromoacetamide 376

Dibromomalondiamide 376-377

2,3-dibromopropyl acrylate (DBPA) 317, 378-384, 397-425

2,3-dibromopropyl methacrylate (DBPM) 401-425

Diethylvinylphosphonate (DEVP) 181

Differential thermal analysis (DTA) 30, 32, 35-37, 60, 197, 235,
243, 386-387

Dimethyl 1-acetoxyvinylphosphonate (DAVP) 178, 401, 425

Dimethylallylphosphonate (DMAP) 180

Dimethyl 1-methoxyvinylphosphonate (DMVP) 178

Dimethylphosphonomethylacrylate (DPA) 179, 393-425

Dimethylvinylphosphonate (DVP) 180

DMAP

See: dimethylallylphosphonate

DMVP

See: dimethyl 1-methoxyvinylphosphonate

Dow Chemical Co. 327

Dow Corning Emulsion [®] 1111 285

DPA

See: dimethylphosphonomethylacrylate

DTA

See: differential thermal analysis

E. I. Dupont de Nemours 23-24, 342, 351

Dur-O-Cryl[®] BL-1 317

Dur-O-Cryl[®] XWC 134

DVP

See: dimethylvinylphosphonate

Electron beam grafting 24

Electron spin resonance (ESR) 159-167

Emery Industries 25, 378

Ethyl Corp. 23-24, 181, 193, 356, 359, 360

Ethylene dibenzoate 57-58

Ethylene glycol 58

Fireaway[®] 2 382-383

Firemaster[®] 200 118

FF 5-74 77, 81-82, 104, 113-120, 174, 208, 212, 253, 256, 285,
290-301, 312, 317, 378, 380-383, 393

Flame Snub Intermix[®] 118

FMC 23-24, 69

Fyrol[®] 76 24, 110, 115, 194, 377, 394-425

Fyrol[®] BB 197, 197, 201, 397-425

Gas chromatograph pyrolysis 131-133

Glo-tard[®] PE-10 118

Glyoxal resins

See: Permafresh[®] 113B

Permafresh[®] LF

Grafting 69, 174, 393-425

Grafting $^{60}\text{C}_\delta$ 181

Graniteville Corp. 25, 378-379

Great Lakes Chem. Corp. (Cavedon) 23-24, 193, 322

H_6
See: 1-(1,2,3,4,7,7-hexachlorobicyclo{2.2.1}-2-hepten-5-yl)-ethene

HBr evolution 141

"Hexa"
See: 1-(1,2,3,4,7,7-hexachlorobicyclo{2.2.1}-2-hepten-5-yl)-ethene

Hexaallyloxyphosphazene 242-243

Hexaallylphosphazine 76-78

1-(1,2,3,4,7,7-hexachlorobicyclo{2.2.1}-2-hepten-5-yl)-ethene
401-425

Hexachlorocyclotriphosphazene 244

Hexamethylphosphorictriamide 182

Hexakis(2,4,6-tribromophenoxy)cyclotriphosphazene 242

Hexaphenoxyposphazene (PFR-1[®]) 157, 171

Hooker Chemicals & Plastics Corp. 11, 177, 180-181, 191, 193, 266,
356, 393, 396

Infra-red 242-243, 245, 257

Isoperibol calorimeter 37, 50-54, 62, 84, 89-104, 107-112, 134,
217-219, 223, 226-229, 233-234, 246-248, 268, 270-272, 276, 278-279,
283-284, 304, 359-375, 389, 391-392

Levi Strauss Inc. 23

Lowenstein Textile Corp. 23, 25, 378

Lyofix[®] CHN 293-294

Match test 62

MAFT

See: Mushroom Apparel Flammability Test

MCC-100[®] 208, 257-259, 267, 289

MCC-100/200/300[®] 249, 251-252, 341-342

MDMP

See: N-methylol-3-(dimethylphosphinyl)prionamide

MD3P

See: N-methylol-3-(diphenylphosphinyl)prionamide

Melamine resins

See: Aerotex[®] 23

Lyofix[®] CHN

2-Methyldioxolane 58

Michigan Chem. Co. 23

Mobile Chemical Co. 23

Monomers for grafting 193

Monsanto Chem. Co. 23

Mushroom

See: Mushroom Apparel Flammability Test

Mushroom Apparel Flammability Test (MAFT) (Mushroom) 81-82, 94,
104, 107-113, 312, 378

N-(dimethylphosphonomethyl)acrylamide (NDPA) 177, 393-425

NDPA

See: N-(dimethylphosphonomethyl)acrylamide

N-methylolacrylamide 358

N-methylol-bis(2,3-dibromopropyl)phosphonoprionamide 71

N-methylol-3-(diallylphosphono)-prionamide 75

N-methylol-3-(dimethylphosphinyl)prionamide (MDMP) 242

N-methylol-3-(dimethylphosphono)propionamide 75
 See: Pyrovatex CP[®]
 N-methylol-3-(diphenylphosphinyl)propinamide (MD3P) 84, 86, 219-240
 N. C. State Univ. 24, 399
 Nuclear Magnetic Resonance (NMR) 242-243, 257-269
 Nyacol, Inc. 23
 OBBP
 See: octabromobiphenyl
 Octabromobiphenyl 130, 134
 Oligomer (precondensate) 208, 212, 257-303
 See: Fireaway[®]
 Pyroset TKS[®]
 Pyrovatex 3762[®]
 THPC[®]
 THPOH
 THPS[®]
 2-oxo-2-methoxy-1,3,2-diazaphosphorinane 242
 Oxygen index 28, 63, 66, 67, 70, 75, 79, 82, 85-86, 113-120,
 215-217, 219-220, 223, 228, 243-244, 249, 251, 256, 358-359,
 361, 375, 378, 397, 398, 400, 407-420, 422, 425
 Oxygen index bottom ignition 82-84, 215, 223
 Oxygen index of PET 122, 125, 127
 Oxygen index vs atmosphere 35, 62
 Oxygen index vs chimney temperature 31, 72-74
 Oxygen index vs moisture content 28-29
 P-44[®] 91-92, 97, 101-103, 117, 143, 304, 308, 312, 317, 366-375
 P-53[®] 370-375
 C. H. Patrick & Co. 25, 378

PCHDT

See: poly(1,4-cyclohexylenedimethyleneterephthalate)

PCPM

See: pentachlorophenylmethacrylate

P(DBPA)

See: poly(1,2,3-dibromopropylacrylate)

Pentabromobiphenylene oxide 322

Pentachlorophenylmethacrylate (PCPM) 401-425

Permafresh[®] 113B 312

Permafresh[®] LF 317

Pert diagrams 9-21

American Enka Res Plan 10

Clemson Univ. Res Plan 15

Hooker Res Plan 11

Polytechnic of NY Res Plan 12

RTI Res Plan 14

SRRC Res Plan 13

Univ. of Maryland Res Plan 15

PET bromine on 127, 143, 155

PET carboxy end group concentration 120-121

PET copolymers 145

PET decomposition kinetics 151-153

PET degradation mechanism 56

PET graft properties 202

PET melt blend additives 145

PET oxidative weight loss 149-150

PET phosphorus on 143-149

PFR-1[®]

See: Hexaphenoxyposphazene

Phenylphosphonyl di(methylbenzoate) 145
 Phenylphosphonyl di(p-methyloxybenzoate) 145
 Phosphazene 69, 172, 242-244
 See: PFR-1
 Sandoz 1030
 Phosphonates 42-43, 63-67
 Phosphoramides 40, 43
 See: MCC-100 (R)
 Phosphoric acid 33-42, 52, 54, 91-92, 242, 258, 282, 363
 Pittsburg Plate Glass Ind. 23
 Poly(1,4-cyclohexylene dimethyleneterephthalate) (PCHDT) 44-47
 Poly(2,3-dibromopropylacrylate) 317
 Polytechnic Institute of New York 12, 120, 143
 Polyvinylbromide (PVBr) 79-80, 91, 130, 134, 356-366, 370, 375,
 377, 378, 397, 398)
 Polyvinylbromide/polyvinylchloride copolymer P(VBr/VCl) 91, 93,
 104-107, 356-366, 370, 375, 377-380
 Precondensate
 See: oligomer
 PVBr
 See: polyvinylbromide
 P(VBr/VCl)
 See: Polyvinylbromide/polyvinylchloride copolymer
 Pyrolysis 33, 35, 87-88, 131-133
 Pyroset (R) TK-115 116
 Pyroset (R) TKS 114
 Pyrovatex (R) 3762 75-76, 84, 86, 108, 246, 250, 255, 256, 271, 272
 Pyrovatex (R) CP 104, 106, 240, 246, 249-250, 255-256, 272, 378

Rate of heat release 53-54, 63, 98, 100, 270-276
 Research Triangle Institute 14, 24, 127, 177
 Riegel Textile Corp. 23
 Sandoz 1030 385-392
 Sandoz Colors & Chemicals 23-24, 385
 Scanning electron micrographs (SEM) 183-189, 385, 407
 SEM
 See: scanning electron micrographs
 Silicone softeners, reactive
 See: Dow Corning Emulsion 1111
 Sodium allylate 243
 Southern Regional Res Center 13, 79-80, 243, 257, 270, 273, 312,
 317, 356, 359-360, 384
 Springs Mills, Inc. 23, 360
 Static oxygen bomb 37, 44, 52, 84, 89-90, 223-225, 229, 232, 246,
 249, 268, 270-276
 Stauffer Chem 145
 J. P. Stevens & Co. 23
 Sun Chemical Co. 23
 Tanatard[®] DN-2 118-120
 Chas. Tanner 23, 25, 317, 378
 TBBPA
 See: tetrabromobisphenol A
 TBPA
 See: 2,4,6-tribromophenylacrylate
 TBPM
 See: 2,4,6-tribromophenylmethacrylate

TBPOEA

See: 2,4,6-tribromophenoxyethylacrylate

TBPOEMA

See: 2,4,6-tribromophenoxyethylmethacrylate

TBPP

See: tris(2,3-dibromopropyl)phosphate

Tennessee Eastman Co. 23

Terephthalic acid 58

Tetrabromobisphenol-A 69

Tetrabromobisphenol A bis(2,3-dibromopropyl) 129-130

Tetrabromobisphenol A bis(hydroxyethyl)ether 127

Tetrakis(hydroxymethyl)phosphonium chloride

See: THPC[®]

Tetrakis(hydroxymethyl)phosphonium sulfate

See: THPS[®]

TGA

See: thermogravimetric analysis

Thermal stability of bromine flame retardants 208-209

Thermal stability of polymer units 211

Thermogravimetric analysis (TGA) 37, 60, 120, 122-124, 139, 141, 149,
197, 229, 235-239, 376, 386, 388, 400, 405-406

THP

See: trihydroxymethylphosphine

THPC[®] 75, 243, 257-260, 266, 272, 289, 321, 356-366, 375-381

THPC[®]/amide 70, 76-79, 114

THPC[®]-APO 71-72

THPC[®]/Diamine 108

THPC[®]/hexaallylaminocyclotriphosphazene 245

THPC[®]/hexamethylaminocyclotriphosphazene 245
 THPC[®]/MCC-100[®] 108, 259, 263, 265-266, 268-269, 273, 277-279, 285-288, 290, 296
 THPC[®]/MCC-100/200/300[®] 110, 273, 278-279, 285, 288, 295
 THPC[®]-McNH₂ 108, 259, 262, 265, 269, 275-276, 282, 284-285
 THPC[®]/Pyrovatex[®] 4013 108
 THPC[®]/tetrachlorodiaminocyclotriphosphazene 245
 THPC[®]-urea 79-80, 91, 93, 114, 255-256, 270, 272-273, 283
 THPOH 261, 265, 268
 THPOH/amide 71, 73
 THPOH/ammonia 38-39, 52, 71, 74, 91-92, 110, 114, 363
 THPOH/MCC-100[®] 108, 259, 264-266, 269, 274, 294
 THPS[®] 208, 266, 289
 THPS[®]/carbamate/200 301-302
 THPS[®]/MCC-100[®] 283, 291, 293, 298-300
 THPS[®]/urea 356, 378-379, 384
 Toyobo, Inc. 23-24, 289
 T23P
 See: tris(2,3-dibromopropyl)phosphate
 TPP
 See: triphenylphosphate
 TPPO
 See: triphenylphosphineoxide
 Triallylphosphate 243, 328
 Triazaphosphaadamantane 242
 2,4,6-tribromophenol 130
 2,4,6-tribromophenoxyethylacrylate (TBPOEA) 317, 378, 393-425

2,4,6-tribromophenoxyethylmethacrylate (TBPOEMA) 327
 2,4,6-tribromophenylacrylate (TBPA) 394-425
 2,4,6-tribromophenylmethacrylate (TBPM) 394-425
 Trihydroxymethylphosphine (THP) 259
 Trimethylphosphoramidate
 See: MCC-100 ^(R)
 Triphenylphosphate (TPP) 44-48
 Triphenylphosphine oxide (TPPO) 37, 39, 42, 60, 62, 65
 Tris
 See: tris (2,3-dibromopropyl)phosphate
 Tris(2,3-dibromopropyl)phosphate (TBPP) (T23P) (Tris) 44-48, 70,
 75, 78-79, 84-85, 91, 93, 328, 329, 334, 375
 Union Carbide Corp. 23
 United Merchants 25, 317, 358, 378
 Univ. of Maryland 15, 24, 268, 356
 VBr₂
 See: vinylidenebromide
 Vertical test 77, 81-82, 104, 113-120, 174, 208, 212, 253, 256,
 285, 290-301, 312, 317, 378, 380-383, 393
 Vinyl benzoate 57
 Vinylidene bromide (VBr₂) 378, 401
 West Point Pepperell Co. 23
 White Chemical Co. 24, 143, 193, 312
 X-ray analysis 184, 187-189, 308, 310

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